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A SYSTEMATIC SCHEME OF QUALITATIVE ANALYSIS FOR ANIONS. III

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In the present scheme[1] for the systematic analysis of anions, two new reagents have been introduced for the separation of anions into groups, namely, zinc nitrate or acetate and cadmium nitrate. The first precipitates a large number of anions and basic radicals which are separated into sub-groups by the use of other reagents. A systematic investigation was undertaken to determine the completeness of the precipitation of the anions and basic radicals by the group reagents. In those cases in which the anion is not completely precipitated but divides itself between the precipitate and the filtrate, the investigation roughly showed the distribution of the anions under these conditions.

METHOD

The method adopted in investigating the completeness of precipitation in the case of anions and basic radicals is described below.

A measured volume of a standard solution of the anion was treated with the group reagent, the precipitate was filtered off, dissolved in acid and the amount of its contained anion was estimated by the same method which was adopted in standardizing the solution. In cases where the solution of the anion was treated with sodium sulphide reagent, any acid present in the solution was neutralized with NaOH solution. In the case of basic radicals, the salt containing the basic radical was boiled with 10% sodium carbonate solution and the mixture filtered. One measured portion of the sodium carbonate filtrate was treated directly for the estimation of the basic radical. Another measured portion was first treated with a slight excess of zinc acetate solution, the precipitate filtered off and the basic radical it contained was estimated by the same method.

The results of this investigation are shown in Table I.

It can be seen from this table that arsenate, tellurate, tellurite, tungstate, selenite and phosphite are quantitatively precipitated by zinc acetate and selenate by cadmium nitrate. Therefore, these two reagents can be utilized for the gravimetric estimation of these anions. Detailed methods for their gravimetric estimations are being developed and may provide convenient and accurate methods for the estimation of many elements in the form of anions. Some of the anions precipitated completely by the group reagents in the scheme of qualitative analysis of anions, have not been included in this investigation; their methods of estimation using these reagents are already well-known.

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TABLE I

Salt solution employed	*Standardized and estimated as*	*% error*
	Precipitation of anions by zinc acetate	
Potassium tellurate	TeS_3 [2]	±0.2 to 0.3
Potassium tellurite	TeS_2 [3]	±0.2 to 0.3
Potassium antimonate	Sb_2S_5 [4]	−0.1
Potassium antimonite	Sb_2S_3 [5]	±0.2
Potassium selenite	SeS_2 [3]	−0.4
Potassium periodate	Volumetrically	−0.8
Sodium arsenate	As_2S_5 [3]	±0.2
Sodium tungstate	WO_3	±0.3 to 0.4
Sodium phosphite	$(NH_4)_3PO_4 \cdot 12MoO_3$	±0.2
Sodium stannate	SnO_2	±0.3
		Percentage which passes into the filtrate
Sodium molybdate	$MoS_3 \cdot 2H_2O$ [6]	60.0
Potassium chromate	Volumetrically	80.0
Potassium arsenite	Volumetrically	10.0
	Precipitation of anions by cadmium nitrate	
Potassium selenate	Se_2S_5 [2]	±0.2
		Percentage which passes into the filtrate
Potassium iodate	Volumetrically	50.0
Potassium chromate	Volumetrically	80.0
	Precipitation of basic radicals in the sodium carbonate filtrate by zinc acetate	
Aluminium	Al_2O_3	+0.2 to 0.3
Beryllium	BeO	−2.0
Zirconium	ZrP_2O_7	+0.3
Thorium	$Th(IO_3)_4$	±0.3
Uranium	U_3O_8	−0.3
Copper	Volumetrically	−0.8
Cobalt (in presence of NH_4 salts)	Co_3O_4	−1.5
Nickel (in presence of NH_4 salts)	$Ni(C_4H_7O_2N_2)_2$	−1.6

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SUMMARY

The completeness of precipitation of anions and basic radicals by the two group reagents, zinc acetate and cadmium nitrate, has been investigated. It has been shown that the two reagents precipitate many of the anions quantitatively and can thus be used for their gravimetric estimation.

RÉSUMÉ

Deux réactifs, l'acétate de zinc et le nitrate de cadmium, sont proposés pour la précipitation quantitative de nombreux anions, pouvant permettre un dosage gravimétrique.

ZUSAMMENFASSUNG

Die quantitative Fällung zahlreicher Anionen mit den Gruppen-Fällungsmittel Zinkacetat und Cadmiumnitrat wurde untersucht.

REFERENCES

[1] I. K. TAIMNI AND MANOHAR LAL, *Anal. Chim. Acta*, 17 (1957) 367, 372.
[2] G. B. S. SALARIA, *Anal. Chim. Acta*, 15 (1956) 514.
[3] I. K. TAIMNI AND R. P. AGARWAL, *Anal. Chim. Acta*, 9 (1953) 121.
[4] G. B. S. SALARIA, *Anal. Chim. Acta*, 17 (1957) 395.
[5] I. K. TAIMNI AND R. P. AGARWAL, *Anal. Chim. Acta*, 10 (1954) 312.
[6] I. K. TAIMNI AND R. P. AGARWAL, *Anal. Chim. Acta*, 9 (1953) 203.

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A SYSTEMATIC STUDY OF INSOLUBLE SUBSTANCES. III

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In a series of papers[1-3] originating from this laboratory, many substances have been discussed which become resistant towards the solvent action of concentrated acids on heating to a high temperature. None of the tungstates, tellurates and vanadates have so far been included in the list of insoluble substances, but investigations carried out in this laboratory have shown that the metal salts of these acids, when heated to 800° for 2 h in a muffle furnace, are hardly soluble in acids.

Tungstates

The general method followed in the preparation of the tungstates consisted of adding an aqueous solution containing the chloride or sulphate of the metal to a hot dilute aqueous solution of normal sodium tungstate, Na_2WO_4. The precipitated tungstates were filtered, washed with water and heated at 800° in a muffle furnace for 2 h. Before the heated tungstates were subjected to the standard acid treatment, they were treated with dilute hydrochloric acid and sodium carbonate solution, successively, to dissolve the oxide of the metal and tungstic acid. The portion of the heated tungstate which dissolves in the standard acid treatment yields a precipitate of tungstic acid. This must be dissolved by washing firstly with a dilute solution of sodium carbonate and then with water containing a small amount of hydrochloric acid before weighing the remaining undissolved portion. Copper tungstate melts at high temperatures and thus was heated on the blow-pipe flame.

The insoluble tungstates were also analysed to determine their percentage composition. Weighed amounts of the heated tungstates were fused with caustic soda (adding potassium nitrate in the case of chromium salt) and the two metals were estimated by the well-known methods. The composition of the heated tungstates was found to be the same as that of the normal tungstates (anhydrous) reported in the literature[4] except in the case of the tungstates of chromium and zirconium. This is evident in the accompanying table.

In regard to the tungstates of Ca, Sr, Ba, Cd, Mn, Al and U, no appreciable change

TABLE I

Name of compound	*Percentage left undissolved in*				*0.01 g of the substance in 1 standard acid treatment*	*Formula given in literature*	*Formula found experimentally*
	2-h ignition at 800°		*9-h additional ignition at 800°*				
	1 standard acid treatment	*5 standard acid treatments*	*1 standard acid treatment*	*5 standard acid treatments*			
Tungstates							
1. Nickel tungstate	98.5	95.2	99.2	96.0	Does not dissolve completely	$NiWO_4$	$NiWO_4$
2. Cobalt tungstate	78.5	56.3	78.5	61.0		$CoWO_4$	$CoWO_4$
3. Chromium tungstate	88.2	76.0	88.2	78.0		$Cr_2O_3 \cdot 2\ WO_3$	$Cr_2O_3 \cdot 1.5\ WO_3$
4. Zirconium tungstate	90.0	88.8	94.2	90.3		—	$2\ ZrO_2 \cdot WO_3$
(5. Zinc tungstate	49.0	29.4	56.5	33.0		$ZnWO_4$	$ZnWO_4$)
(6. Copper tungstate	40.5	12.0	—	—		$CuWO_4$	$CuWO_4$)
Tellurates							
1. Chromium tellurate	99.5	99.0	—	—			
2. Zirconium tellurate	90.0	88.8	92.0	91.5			
Vanadates							
1.,Chromium vanadate	89.5	88.6	—	—			
2. Zirconium vanadate	74.2	71.3	74.2	71.3			

in solubility was found on heating. The tungstates of zinc and copper also dissolved, to a great extent in the standard acid treatment.

Tellurates and vanadates

The behaviour of the tellurates and vanadates of most of the metals was investigated. Though the salts of these acids which dissolve with difficulty are precipitated on mixing solutions of potassium tellurate or ammonium vanadate with the aqueous solutions of these metallic salts, they are not rendered insoluble in acids on heating at a high temperature except in the case of the tellurates and vanadates of chromium and zirconium as shown in Table I. It should be noted that zirconium tellurate is not decomposed by alkaline fusion and has to be fused with potassium acid sulphate as in the case of the oxides of cerium, thorium and rhodium.

To determine to what degree the insoluble compounds would be affected in preparing the sodium carbonate filtrate for the detection of the anions, the heated compounds were boiled with about 10% sodium carbonate solution for 10 min. All the insoluble tungstates, tellurates and vanadates are decomposed slightly, enough to yield a positive result for the anion in the filtrate when testing. The chromites and aluminates reported in an earlier paper[3], and nickel tungstate are not at all affected by this treatment.

Note

The molybdates and selenates of most of the metals were prepared and heated at 900° for 2 h in a muffle furnace but none were rendered insoluble in acids.

SUMMARY

The tungstates of Ni, Co, Cr, Zr, Zn and Cu and the tellurates and vanadates of Cr and Zr, when heated at 800° were found to become sufficiently resistant to the standard acid treatement to be considered insoluble. The tungstates, tellurates and vanadates of other metals were not affected by heating.

RÉSUMÉ

Les tungstates de Ni, Co, Cr, Zr, Zn et Cu, ainsi que les tellurates et vanadates de Cr et Zr, chauffés à 800° deviennent suffisamment résistants à l'attaque par les acides pour être considérés comme insolubles. Par contre, le chauffage est sans influence sur les tungstates, tellurates et vanadates des autres métaux.

ZUSAMMENFASSUNG

Es wird nachgewiesen, dass die Wolframate von Ni, Co, Cr, Zr, Zn und Cu sowie die Tellurate und Vanadate von Cr und Zr durch Erhitzen auf 800° genügend säurebeständig werden, so dass sie als „unlöslich" betrachtet werden können. Die Löslichkeit der Wolframate, Tellurate und Vanadate anderer Metalle wird durch die Hitzebehandlung nicht beeinflusst.

REFERENCES

[1] I. K. Taimni and G. B. S. Salaria, *Anal. Chim. Acta*, 14 (1956) 4.
[2] G. B. S. Salaria, *Anal. Chim. Acta*, 19 (1958) 316.
[3] I. K. Taimni and I. S. Ahuja, *Anal. Chim. Acta*, 19 (1958) 492; 20 (1959) 70.
[4] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. XI Longman's Green and Co., London, 1931, p. 773.

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A STUDY OF THE PURITY AND UNIFORMITY OF COMPOSITION OF FERROUS AMMONIUM SULFATE HEXAHYDRATE AS A SOLID STANDARD REDUCTANT

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The use of ferrous ammonium sulfate hexahydrate (Mohr's salt) as a solid standard reductant has been discouraged because it is not amenable to a high degree of purification by recrystallization[1]. However, when the need arose for a method to assay ultrapure chromium to better than 0.1% on a routine basis, its high equivalent weight and simplicity of reaction with oxidizing solutions made its use seem highly attractive. The advantages of Mohr's salt over arsenious trioxide, an alternate choice of solid reductant which can be obtained in primary standard quality, include the the avoidance of the need for catalysis and the ease of its solubility in acidic solutions. Therefore, the following study of the purity and uniformity of composition of a commercially available analytical reagent was undertaken to determine its suitability for the proposed assay method for chromium metal[2]. It was anticipated that present-day manufacturing processes had sufficiently improved the quality of the available analytical reagent to permit its use as a "secondary" standard material.

As a basis for the following work, primary standard potassium dichromate was used as the fundamental reference of purity. To avoid volumetric errors, weighed quantities of solid reagent-grade ferrous ammonium sulfate hexahydrate were added in slight excess to solutions of known weights of the potassium dichromate. An amperometric titration, adapted from the work of PARK AND LYKKEN[3], was then used to measure the excess ferrous ion.

EXPERIMENTAL

Apparatus and reagents

The amperometric titration was performed in a 600-ml beaker accommodating a rotating platinum microelectrode, and the salt bridge connection from a saturated calomel reference electrode. The salt bridge was conveniently made from Tygon tubing filled with saturated potassium chloride and plugged by means of a short length of porous Vycor which may be obtained from the Corning Glass Works (Glass 7930)[4]. The microelectrode was rotated using a Sargent Synchronous Rotator, S-76485. Voltage was applied and the diffusion currents measured with a Sargent Ampot, S-29710. Stirring was accomplished magnetically using a Teflon-covered stirring bar, and titrations were made from a 10-ml microburet.

The ferrous ammonium sulfate hexahydrate studied was the Analytical Reagent grade supplied by the Mallinckrodt Chemical Works. Both catalog items, 5064 and 5068 ("low manganese" content), were used. Primary Standard, Analytical Reagent, potassium dichromate was also obtained from Mallinckrodt. A 0.0200*N* solution of potassium dichromate was prepared directly from the primary standard material. All other solutions were prepared from analytical grade reagents.

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Procedure

Approximately 1.4 g of primary standard potassium dichromate was accurately weighed, and dissolved in about 300 ml of distilled water. The solution was then acidified with 30 ml 1:1 sulfuric acid and 6 ml of 1:1 nitric acid and cooled to room temperature. A calculated amount of ferrous ammonium sulfate hexahydrate was weighed to the nearest 0.1 mg to provide an excess of about 0.1 milliequivalent greater than the equivalents of dichromate. As a first approximation, the purity of the ferrous ammonium sulfate was assumed to be 100%. The weighed reagent was added directly to the dichromate solution which was then stirred magnetically for approximately 3 min to completely dissolve the salt. After immersing the platinum electrode and connecting salt bridge in the solution $+1.0$ V was applied to the rotating platinum electrode. An anodic current of approximately 30 μA indicated the presence of excess ferrous ion. The initial current was recorded, and the titration was performed in the usual manner using 0.0200N potassium dichromate in 2-ml increments. The current decreased linearly to zero at the end-point. From the total number of milliequivalents of potassium dichromate consumed, and the weight of ferrous ammonium sulfate hexahydrate taken, the purity of the latter was calculated.

RESULTS

In order to evaluate the homogeneity of ferrous ammonium sulfate hexahydrate within a bottle, one pound was carefully quartered without prior mixing, and three assay analyses performed on each quarter. The results, shown in Table I, indicated a remarkable constancy of composition as well as high purity. The standard deviation, representing the total variability of the measurements as well as any variability in the composition of the salt, indicated a precision of about two parts per ten thousand. The reliability of this estimate of precision, calculated by its upper 99% confidence limit, indicated a probability of only one in a hundred that the estimated precision was actually greater than four parts in ten thousand. One may conclude that the material in this bottle was essentially homogeneous and that the method was capable of high precision.

TABLE I

ASSAY (IN %) AND HOMOGENEITY OF A ONE-POUND BOTTLE OF FERROUS AMMONIUM SULFATE HEXAHYDRATE[a] AGAINST PRIMARY STANDARD POTASSIUM DICHROMATE[b]

Quarter[c]	*1*	*2*	*3*	*4*
	99.92	99.89	99.87	99.82
	99.84	99.83	99.84	99.87
	99.87	99.89	99.85	99.86
Average	99.88	99.87	99.85	99.85
Grand average				99.862
99% Confidence limits of grand average				99.841–99.883
Standard deviation of an individual measurement				± 0.023 ($n = 12$)
99% Upper confidence limit of the standard deviation				0.044

[a] Mallinckrodt Catalog #5064.
[b] Mallinckrodt Catalog #6772.
[c] Contents of bottle quartered, without mixing, prior to analysis.

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TABLE II

COMPARISON OF ASSAYS (IN %) AND HOMOGENEITIES OF THREE ONE-POUND BOTTLES OF FERROUS AMMONIUM SULFATE HEXAHYDRATE AGAINST PRIMARY STANDARD POTASSIUM DICHROMATE

Bottle	*1*[a]	*2*[b]	*3*[c]
Average	99.862	99.852	99.871
99% Confidence limits of average	99.841–99.883	99.825–99.879	99.849–99.893
Standard deviation of an individual measurement[d]	±0.023	±0.030	±0.024
99% Upper confidence limit of the standard deviation	0.044	0.057	0.046

[a] Mallinckrodt Catalog #5064; data reported in Table I.
[b] Mallinckrodt Catalog #5064
[c] Mallinckrodt Catalog #5068.
[d] $n = 12$ for each estimate.

Table II shows the results obtained with two additional one-pound bottles of ferrous ammonium sulfate hexahydrate where one of these was the "low manganese" grade of analytical reagent. The same experimental design previously described was used. Included in Table II are the results of the analyses on the first bottle tested (Table I), and a comparison of the three standard deviations indicates the same high degree of homogeneity in each bottle. In addition, the assays of these three individual one-pound quantities were notably the same despite the fact that at least one of them ("low manganese" grade) was purchased as a separate catalog item (5068).

Ten months after the data shown in Table II had been obtained, the hydrate in bottle 2 was re-assayed to detect any change in its reducing power. No special precautions had been taken to safeguard its quality except to keep it stored in the original bottle with its plastic screw cap. Occasional use had been made of this material over this period. Table III summarizes the re-assay data which shows a slight but significant decrease of about 0.05% in its effectiveness as a reductant.

TABLE III

RE-ASSAY OF FERROUS AMMONIUM SULFATE HEXAHYDRATE (Bottle 2, Table II) AFTER A PERIOD OF TEN MONTHS. STUDY OF THE EFFECT OF PHOSPHORIC ACID ON THE AMPEROMETRIC TITRATION

	Phosphoric acid present	*Phosphoric acid absent*
	99.81	99.80
	99.80	99.79
	99.81	99.80
	99.81	99.81
	99.82	99.79
	99.80	99.82
Average	99.808	99.802

Grand average	99.805
99% Confidence limits of grand average	99.795–99.815
Standard deviation of an individual measurement	±0.011 ($n = 12$)
99% Upper confidence limit of the standard deviation	0.021

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In conjunction with this assay, the effect of phosphoric acid, which shifts the oxidation of the ferric-ferrous system in favor of more complete reaction with dichromate, was also studied. As indicated in the table where 6 results were obtained in the presence of phosphoric acid (5 ml of 85% phosphoric acid added to solution prior to titration according to above procedure) and 6 without it, essentially identical assays were obtained in both cases indicating that the use of phosphoric acid is unnecessary with an amperometric end-point.

DISCUSSION AND CONCLUSIONS

Although the work reported is necessarily a very limited sampling of the commercially available reagent, it indicates that the Mallinckrodt product, in particular, is suitable with respect to both its high purity and uniformity of composition as a secondary-standard solid reductant. Without extensive evaluation of homogeneity, other one-pound quantities, which were obtained periodically, have also been found to possess essentially the same high purity. In several cases, the appearance of the reagent with respect to its crystallinity would make us suspect that differences in reducing power would be found because of varying water content. However, subsequent evaluation of such lots has not revealed a significant difference in their assay.

SUMMARY

A study of the purity and uniformity of composition of commercially available ferrous ammonium sulfate hexahydrate has been undertaken to determine its suitability as a solid standard reductant. Weighed quantities of reagent-grade Mohr's salt were added in slight excess to solutions of known weights of primary standard potassium dichromate. An amperometric titration was then used to measure the excess ferrous ion. Results found indicate that present-day manufacturing processes have sufficiently improved the quality of the available analytical reagent to permit its use as a secondary-standard solid reductant.

RÉSUMÉ

On a examiné le sulfate double de fer(II) et d'ammonium (sel de Mohr) en vue de son utilisation comme étalon en chimie analytique. Des quantités déterminées de ce réactif ont été ajoutées en léger excès à des solutions de dichromate de potassium titrées. On a mesuré ensuite l'excès de fer(II) par ampérométrie.

ZUSAMMENFASSUNG

Das Eisen-(2)-ammoniumsulfat (Mohr'sches Salz) wurde auf seine Eignung als Standard-Reduktionsmittel für die analytische Chemie untersucht. Gewogene Mengen des Eisen-(2)-Salzes wurden in geringen Überschuss zu einer Lösung mit bekanntem Kaliumbichromatgehalt gegeben und der Überschuss an Eisen-(2)-Salz amperometrisch ermittelt.

REFERENCES

[1] I. M. KOLTHOFF AND E. B. SANDELL, *Textbook of Quantitative Inorganic Analysis*, The Macmillian Co., New York, 3rd Ed., 1952, p. 566.

[2] H. J. KEILY, A. ELDRIDGE AND J. O. HIBBITS, *Anal. Chim. Acta*, 21(1959) 135.

[3] T. D. PARKS AND L. LYKKEN, *Anal. Chem.*, 22 (1950) 1503.

[4] W. N. CARSON, JR., C. E. MICHELSON AND K. KAYAMA, *Anal. Chem.*, 27 (1955) 472.

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THE CONDUCTOMETRIC TITRATION OF CARBOXYLIC AND PHENOLIC ACIDS IN NON-AQUEOUS SOLUTIONS

II. STUDY OF THE TITRATION OF DIBASIC ACIDS

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INTRODUCTION

The conductometric titration of dibasic acids in non-aqueous solvents using tetramethylammonium hydroxide as a base yields conductance curves of various shapes, depending on the acid as well as on the solvent employed[1]. In some solvents the strongest dibasic acids, *i.e.* those in which the ratio of the two ionization constants in water is 100 or more (oxalic, phthalic acid etc.), give N-shaped titration curves, the conductance of the solution showing a minimum at the second equivalence point, not caused by formation of a precipitate. (The occurrence of an N-shaped curve as a result of precipitate formation after the first equivalence point will not be discussed.) In other solvents no minimum is observed with these acids and the titration curve has the shape of a chair. Weaker acids such as isophthalic acid generally show the latter behaviour in all solvents.

In the present investigation the factors determining the shape of the titration curves of dibasic acids in non-aqueous media were studied more thoroughly. Thus titrations with other bases, some of them giving salts which are soluble in most solvents, were performed. The base used by preference was tetra-*n*-butylammonium hydroxide; other bases, less frequently used, were diethylamine and piperidine, and lithium and potassium methoxide.

The factors under consideration are: (1) The distance between the acid groups; (2) The properties of the solvent, in particular: a. the solvating power (presence of groups forming hydrogen bonds, such as —OH); b. the mean dielectric constant; (3) The size of the base cation; (4) The temperature.

From the results of the study of these factors the conditions can be found for producing the most suitable titration curves and hence for obtaining maximum accuracy in the determination of the equivalence points.

EXPERIMENTAL

Solvents and titrants

The purification of the solvents and the preparation of the quaternary ammonium bases were described in the previous paper[1]; tetrabutylammonium hydroxide was made in the same way as the tetramethylammonium hydroxide solution. The strength of the tetrabutylammonium hydroxide solutions used varied between 0.1 *N* and 0.3 *N*, that of the tetramethylammonium hydroxide was 0.1 *N*. The strongest solutions consisted of the hydroxide dissolved in equal parts by volume of methanol and benzene; with the decinormal solutions the methanol–benzene ratio was either 1 : 3 or 1 : 4 (v/v).

For the diethylamine and piperidine titrants we made solutions of the freshly distilled compounds in methanol. The strength of both bases was 0.2 *N*.

The two methoxides were prepared by dissolving the required amount of metal in methanol. The strength of these bases was 0.1 *N*.

Apparatus

In most of the titrations the resistances were measured with the equipment described previously[1]; the relative accuracy was better than 1%. For the titrations with piperidine and diethylamine as titrants, however, the normal apparatus was not sufficiently sensitive, so that at higher resistances the error rapidly increased to 1–5%. Therefore a new bridge was built, which was fed by an audio-frequency oscillator and used a cathode-ray oscilloscope as the zero-point indicator. With this bridge all titrations could be carried out satisfactorily.

For the titrations at higher temperatures a jacketed cylindrical glass vessel closed by a cork plug was used. This plug was provided with holes for the dip-electrode assembly (cell constant $\sim 0.8\ \mathrm{cm}^{-1}$), a thermometer and the burette tip. Water from a thermostat circulating through the cell jacket permitted temperature control to approx. 0.05° at the three temperatures used (25°, 50° and 70°). During titration the solution was stirred with a magnetic stirrer.

Titration procedure

For every titration the acid was brought into the titration vessel, either by weighing the pure compound or by pipetting a standard solution in such a quantity, that about 1 ml of base was required per acid group. Then the volume was made up to 40–60 ml and the solution stirred until it had attained the temperature of the thermostatted vessel. Small portions of base were added (approx. 0.10 ml from a semi-micro burette) and the readings were taken when they became constant. This was normally the case within half a minute.

DISCUSSION OF RESULTS

a. Influence of the distance between the acid groups

The experimental results indicate that in general the dibasic acids, so far as the conductometric titration in non-aqueous media is concerned, may be divided into two groups: those that are able to give N-shaped titration curves, and those that will, under any conditions, only give chair-shaped curves.

The first group comprises the acids for which the K_1/K_2 ratio in water is 100 or more (sulphuric, oxalic, malonic, maleic and phthalic acid), the second group consists of those for which this ratio is lower than 100, in general 10–40 (sebacic acid: 10, adipic acid: 35[2]. (Figs. 1 and 2) (K_1 and K_2 are the first and the second ionization constant, respectively.)

There are a few exceptions to this rule, however: succinic, glutaric, malic and tartaric acid, for instance, which have a K_1/K_2 ratio in water lower than 100, nevertheless give N-shaped titration curves under the same conditions as malonic acid. Hence, as far as titration in non-aqueous media is concerned these acids belong to the first group. The explanation of this phenomenon will be given in a later paper.

The behaviour of adipic and fumaric acid (Figs. 1 and 2) is intermediate between these two groups: in most cases a chair-shaped curve is obtained, but under special conditions (see d.) an N shape is also possible.

From the experiments it can be seen that acids, in which the distance between the carboxylic groups is at least 8 Å[3], give chair-shaped curves only. In the series of the α,ω-dicarboxylic acids this applies to adipic acid and the higher homologues. For isophthalic and terephthalic acid this statement does not hold: these acids give chair-shaped curves although the distance is only 5–6 Å, but here the rigid structure plays an important role. For further details the reader is referred to a forthcoming paper.

b. Influence of solvent

The most important properties of the solvent influencing the titration are its dielectric constant ε and its solvating power.

The first of these will determine the electrostatic forces acting between the ions and hence the degree of ionization of the salts of a dibasic acid[1]. The ionization of the acid salts is, however, less influenced by changes in the dielectric constant than that of the neutral salts. The influence of ε is illustrated in Fig. 3 by the shape of the titration curve of malonic acid in dimethylformamide(DMF)–benzene mixtures, which shows that optimum results with respect to the accuracy in the determination of the intersections are obtained at values of ε below 20, *i.e.* for a DMF/benzene volume ratio below 1 : 1 (the approximate values of ε were calculated on the assumption that $\varepsilon_{\text{solvent}} = x_1\varepsilon_1 + x_2\varepsilon_2$, in which x_n = mole fraction of compound n).

These titrations are complicated, however, by the strongly decreasing conductance of the solutions, hence it will be practically impossible to use DMF/benzene ratios below 1 : 4. For the same reason the use of pyridine–benzene mixtures was unsuccessful.

Similar results are obtained when titrating in alcohol–benzene mixtures with lithium or potassium methoxide (Fig. 4) or with tetramethylammonium hydroxide. In these systems the amount of benzene also determines the conductance of the solutions to a great extent.

The second property of the solvent, its solvating power, is more important than the first. In pure methanol, for instance, it is impossible to obtain N-shaped titration

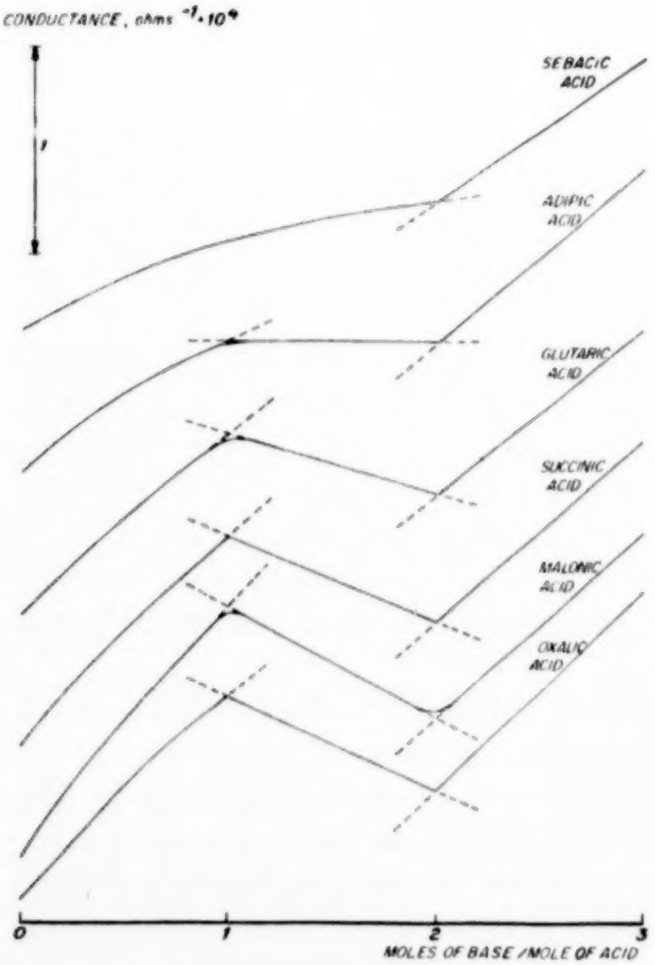

Fig. 1. Titration of *α, ω*-dicarboxylic acids in pyridine with tetrabutylammonium hydroxide (curves have been shifted vertically for clarity).

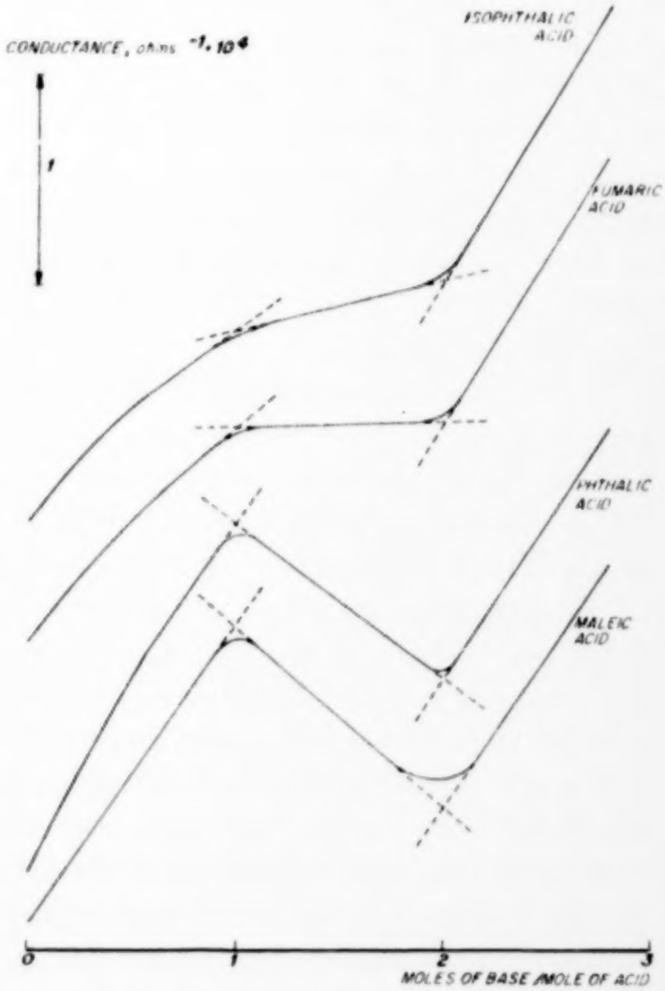

Fig. 2. Titration of some dicarboxylic acids in pyridine with tetrabutylammonium hydroxide (curves have been shifted vertically for clarity).

curves when using quaternary ammonium bases, whereas in pure propanol-2, as a consequence of its lower solvating power, N-shaped curves are often found when tetramethylammonium hydroxide is used. As a matter of fact, the decrease in dielectric constant, if one goes from methanol ($\varepsilon_{25} = 32.6$) to propanol-2 ($\varepsilon_{25} = 18.3$), partly accounts for the change in behaviour. The solvating properties of the solvent are predominant, however, as is clearly proved by the titration of phthalic acid with tetrabutylammonium hydroxide in methanol–benzene (1 : 3 v/v); this solvent has approximately the same dielectric constant ($\varepsilon \approx 13$) as pyridine, but as a consequence of the methanol present no N-shaped curve could be obtained in it. In non-solvating media such as pyridine and DMF, N-shaped curves may be obtained more often and hence these solvents are to be preferred for analytical purposes.

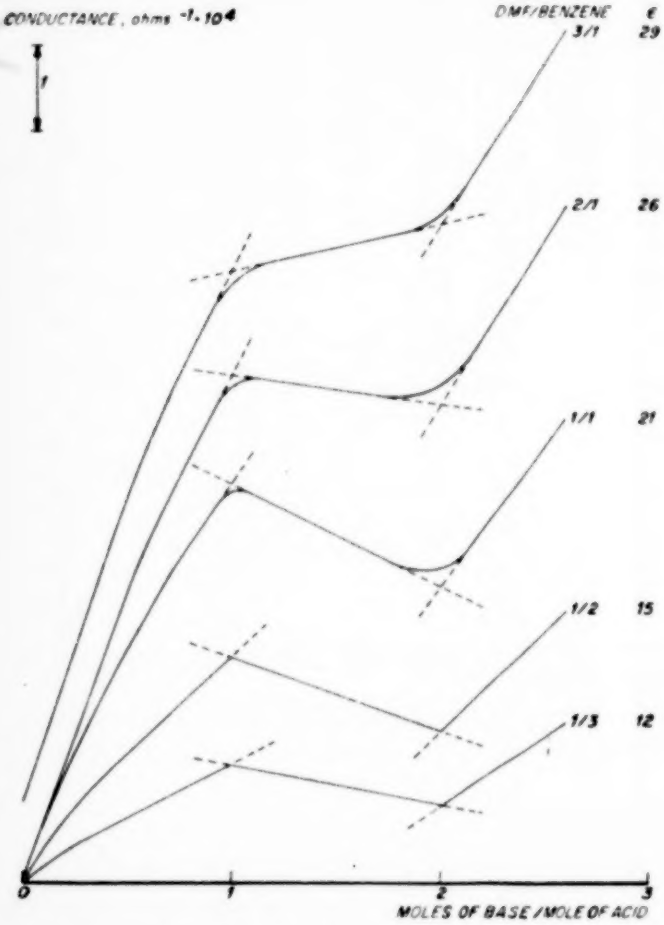

Fig. 3. Titration of malonic acid in DMF–benzene mixtures of different ratios (v/v) with tetrabutylammonium hydroxide (curves have been shifted vertically for clarity).

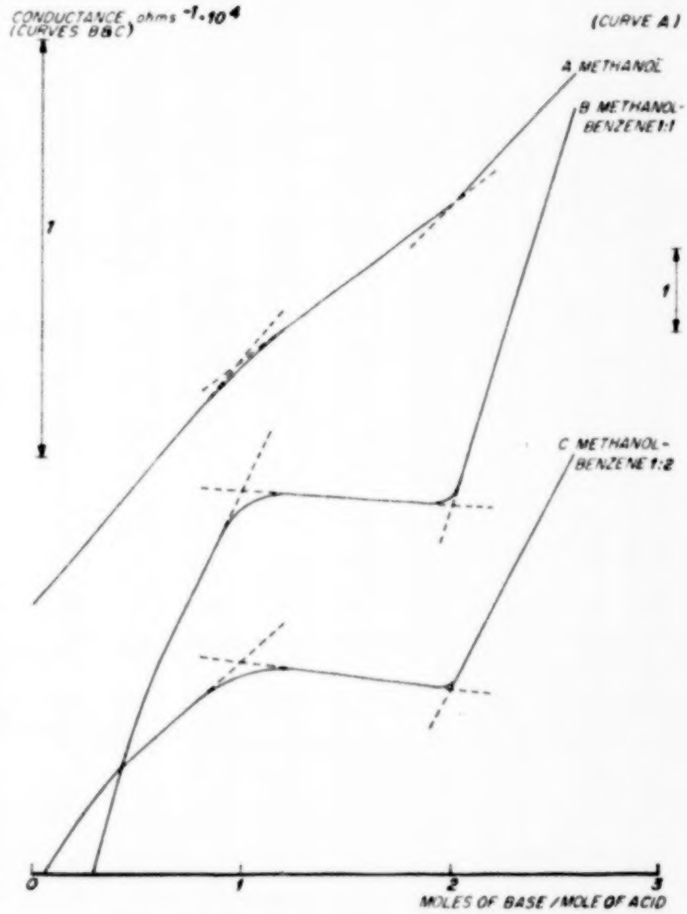

Fig. 4. Titration of succinic acid in methanol–benzene mixtures of different ratios (v/v) with potassium methoxide (curves have been drawn on different scales and have been shifted vertically for clarity).

c. Influence of base cations

It has often been observed that one base gives titration curves very different from those obtained with another. An example of this phenomenon is shown in Fig. 5, representing the titration of phthalic acid in methanol with tetramethyl- and tetrabutylammonium hydroxide and with piperidine. Similar results are obtained in alcohol–benzene mixtures with lithium or potassium methoxide (*cf.* Fig. 4 and ref. 4).

Titration of dibasic acids should, according to this evidence, preferably be carried out with bases derived from small cations (Li^+, K^+, Me_4N^+) or with amines. The applicability of such bases is, however, limited, as in most cases neutral salts of these bases and dibasic acids are insoluble in non-solvating media such as pyridine and DMF. The solubility of the lithium and potassium salts formed is low even in some solvating media such as propanol-2 and some methanol–benzene mixtures. It should further be mentioned that in most titrations carried out in alcoholic media the equivalence points cannot be determined accurately as a result of solvolysis. The changes in conductance in titrations with amines are in general too small for reliable determinations.

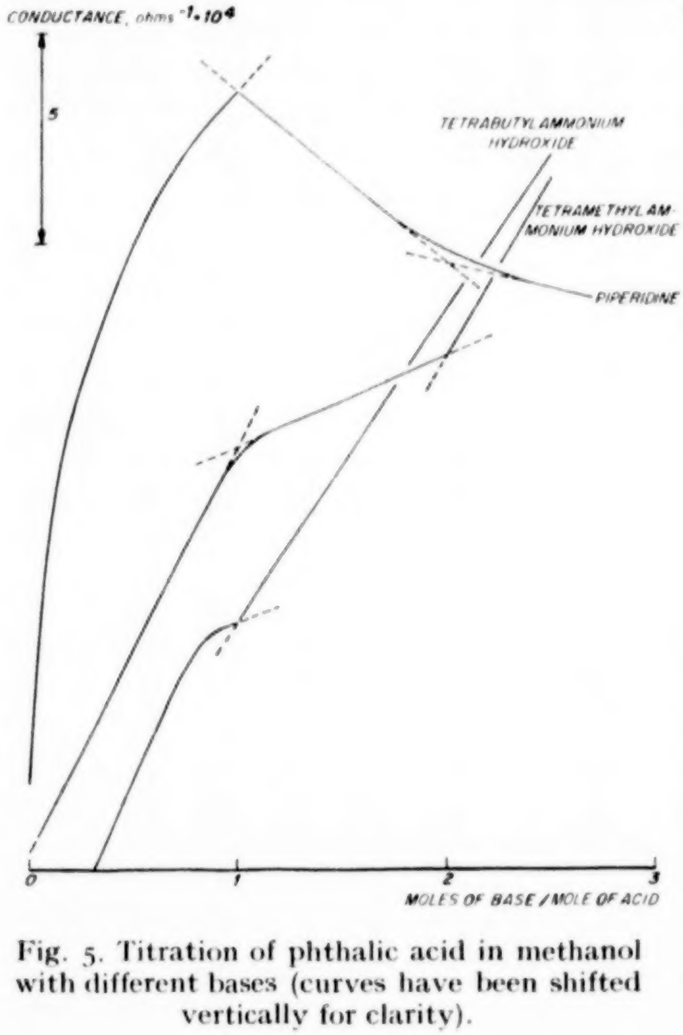

Fig. 5. Titration of phthalic acid in methanol with different bases (curves have been shifted vertically for clarity).

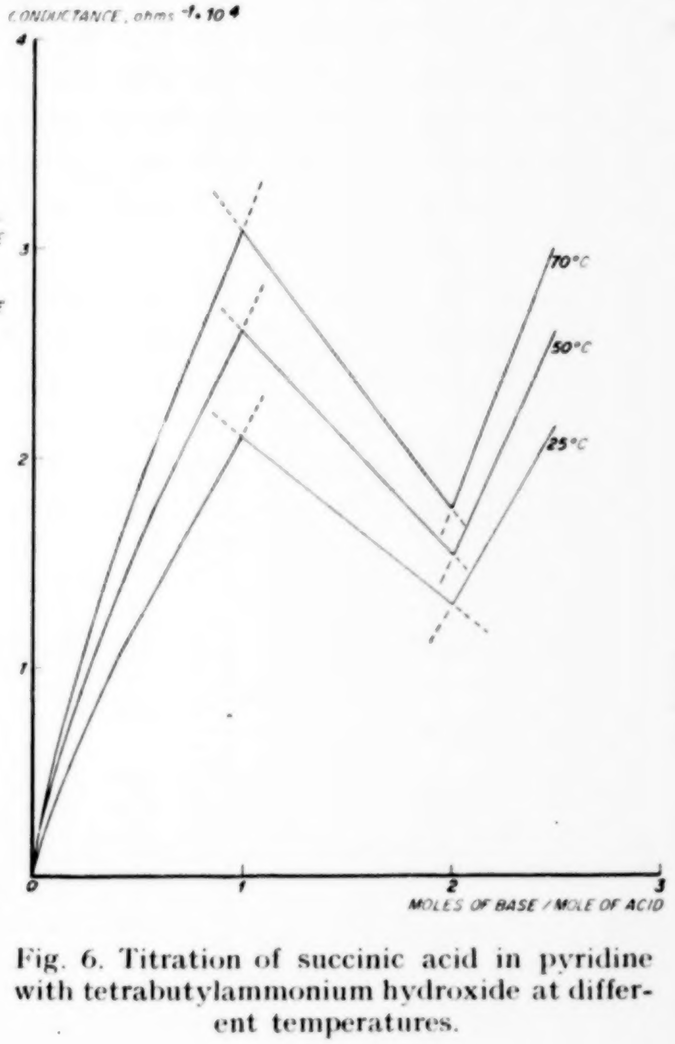

Fig. 6. Titration of succinic acid in pyridine with tetrabutylammonium hydroxide at different temperatures.

Summarizing, the base giving the best analytical results is tetrabutylammonium hydroxide, provided the titrations are carried out in non-solvating media of fairly low dielectric constant. Such titrations, especially in mixtures, will be dealt with in a future paper.

d. Influence of temperature

If the titrations are performed at higher temperatures the shapes of the curves are significantly changed for some acids, whereas for others there is hardly any temperature influence apart from an overall increase in conductance.

Figs. 6, 7 and 8 illustrate the temperature effect. Fig. 6 shows the titration curve of succinic acid in pyridine with tetrabutylammonium hydroxide at 25°, 50° and 70° (the other members of the first group of acids — *cf.* a. — give similar curves).

No pronounced change in shape takes place as the temperature is raised except that the N shape becomes just a little sharper.

Nor does the chair-shaped curve of isophthalic acid alter under these circumstances (Fig. 7). In the case of fumaric and adipic acid, however, a definite change was noted, the curve turning from chair-shaped at 25° to weakly N-shaped at 70° (Fig. 8). One observes similar effects in alcoholic media when titrating with other bases, *e.g.* in methanol–benzene (1 : 1 v/v) with lithium or potassium methoxide or in propanol-2 with tetramethylammonium hydroxide.

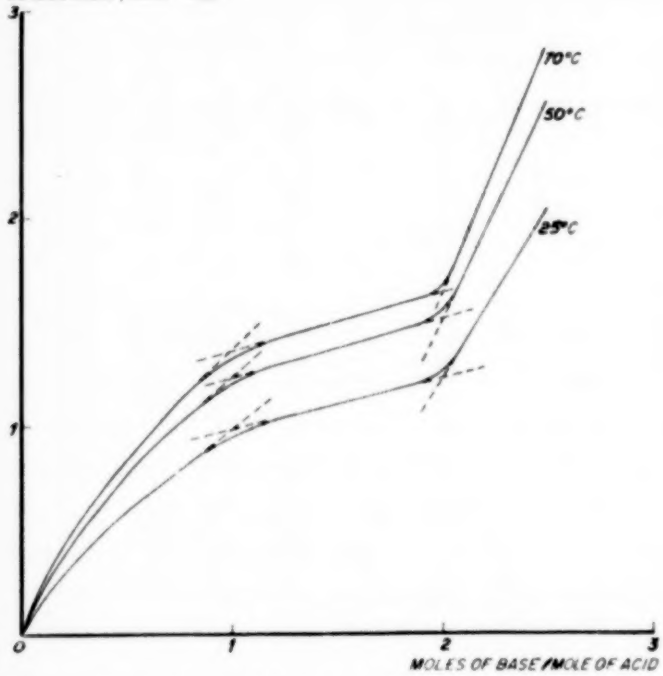

Fig. 7. Titration of isophthalic acid in pyridine with tetrabutylammonium hydroxide at different temperatures.

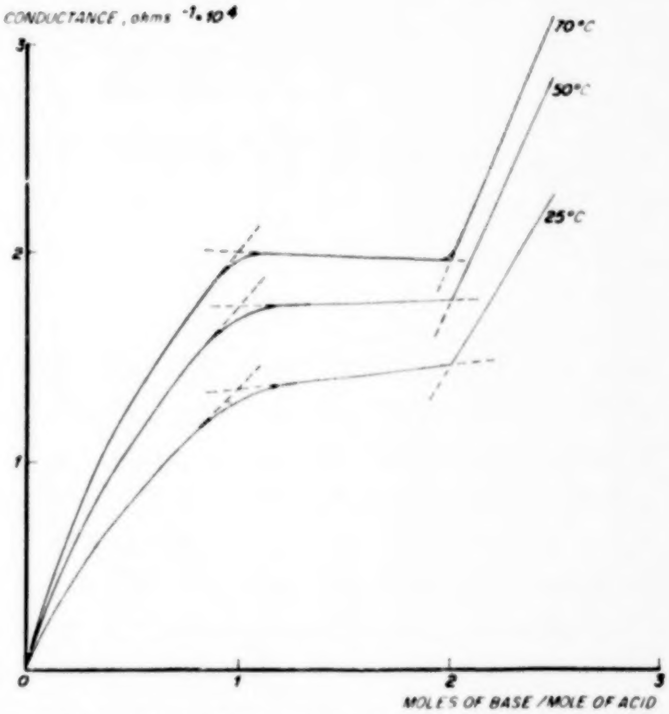

Fig. 8. Titration of adipic acid in pyridine with tetrabutylammonium hydroxide at different temperatures.

The change in the shape of the titration curves is not, as might be supposed, caused by the decrease in the dielectric constant of the solvent. The ε value of pyridine decreases from 12.3 at 25°[5] to about 10.8 at 70°. A mixture consisting of 5 vol. of pyridine and 1 vol. of benzene has the same ε value at 25°. Titration of adipic, fumaric and isophthalic acid in this solvent at room temperature showed that the decrease in ε at 25° does not affect the shape of the titration curves in the same way as does the rise in temperature by 45 degrees (Fig. 9).

The explanation of this temperature influence will be given in a forthcoming paper.

From the experiments it is seen that for analytical purposes (accurate determination of the equivalence points) it may be profitable to titrate at higher temperatures.

CONCLUSIONS

From the experiments described it can be concluded that for the conductometric titration of dibasic acids media of low solvating power and with a low dielectric constant are to be preferred. Of the titrants investigated tetrabutylammonium hydroxide gave the best results.

Titration at higher temperatures, up to 70°, in some cases increases the accuracy in the determination of the end-points.

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ACKNOWLEDGEMENT

The authors are much indebted to Miss A. SNIP and the late Mr. P. J. LAFARGUE who skilfully carried out many of the experiments. They also wish to express their gratitude to Dr. Ir. P. N. DEGENS, Jr. for his stimulating interest in this investigation.

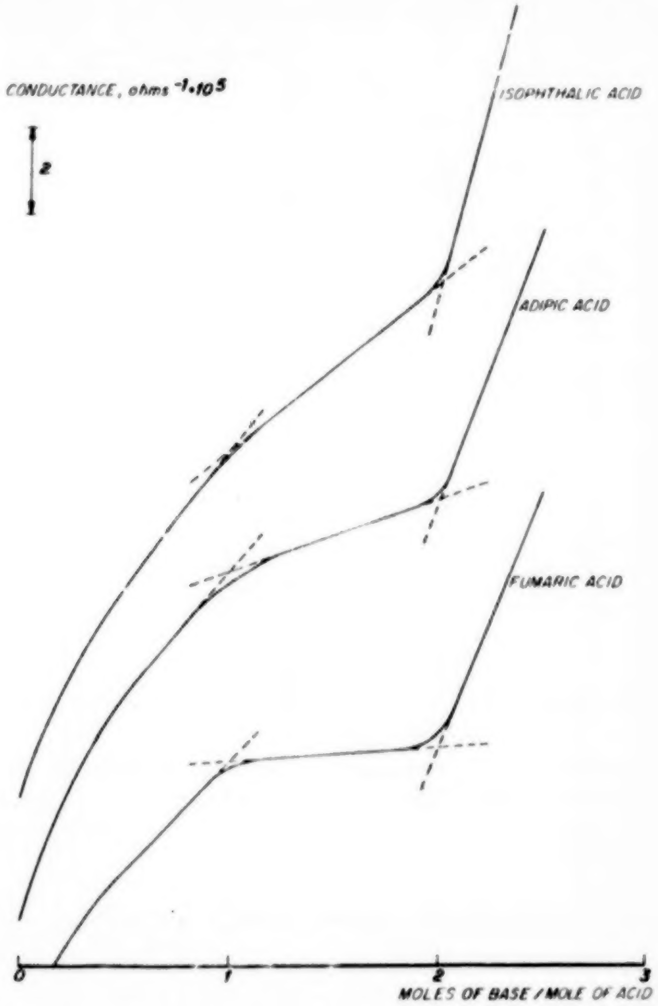

Fig. 9. Titration of adipic, fumaric and isophthalic acid in pyridine–benzene (5 : 1 v/v) with tetrabutylammonium hydroxide (curves have been shifted vertically for clarity).

SUMMARY

An experimental study has been made of the conductometric titration of dibasic acids in non-aqueous solvents.

The factors governing the shape of the titration curve and hence determining the accuracy of the analysis of these compounds are discussed, and the conditions are given under which optimum results are obtained.

RÉSUMÉ

Une étude expérimentale a été effectuée sur le titrage conductométrique des acides dibasiques en solvants non-aqueux.

ZUSAMMENFASSUNG

Es wird über ein konduktometrisches Titrationsverfahren zur Bestimmung zwei-basischer Säuren in nicht-wässrigem Lösungsmittel berichtet.

REFERENCES

[1] N. VAN MEURS AND E. A. M. F. DAHMEN, *Anal. Chim. Acta*, 19 (1958) 64.

[2] M. L. DONDON, *J. chim. phys.*, 54 (1957) 290, 304.

[3] M. MASUI AND T. TESHIMA, *Pharm. Bull. (Tokyo)*, 3 (1955) 446.

[4] M. MASUI AND Y. BAN, *J. Pharm. Soc. Japan*, 77 (1957) 1111.

[5] *Table of Dielectric Constants of Pure Liquids*, Natl. Bur. of Standards, Circular No. 514 (1951).

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VOLTAMMETRIC, POTENTIOMETRIC AND AMPEROMETRIC STUDIES WITH A ROTATED ALUMINUM WIRE ELECTRODE

I. VOLTAMMETRIC BEHAVIOR OF THE R.AL.E.

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The aluminum electrode is a highly polarizable electrode both anodically and cathodically, the passivity of the metal being attributed to a film of aluminum oxide covering the electrode surface. The electrode potentials measured by electrochemical techniques do not agree with the values calculated from thermodynamic data. Based on free energy data, LATIMER[1] calculated the standard electrode potential for the reaction: $Al = Al^{+3}$ (aq.) + 3e to be equal to —1.66 V *versus* the normal hydrogen electrode. However, potential measurements at a "pure" aluminum electrode give values which are much less negative than those corresponding to the above standard potential. Using an aluminum amalgam electrode, HEYROVSKY[2] calculated a value for the electrode potential of —1.337 V with reference to the normal hydrogen electrode.

The use of aluminum sheet (99.99% pure) as a pH-indicator electrode has been recommended by SCARANO[3] in potentiometric titrations of acids with bases. Reponse to pH, however, has not been reported. It is only stated that a large break in potential occurred at or near the equivalence point, but no potential data are reported in solution of a given pH.

After completion of our work, PLUMB[4] using electrodes which were made free of oxide by scraping the surface with alumina, reported values ot potentials after different periods of time in oxygen-saturated solutions of various pH. He extrapolated the values to zero time (zero oxide thickness) and considered them to correspond to the potentials of the oxide-free electrode. The potentials thus obtained differed by more than 0.6 V from the values calculated on the basis of LATIMER's standard potential. PLUMB offers an interpretation for this discrepancy. It should be realized, however, that the anodic reaction at an aluminum electrode differs from the cathodic reaction and the potential therefore does not correspond to that of a reversible system.

According to our findings, in acid medium a pure aluminum electrode does not function as a pH electrode. In agreement with PLUMB it was found that the potentials in solutions containing excess of hydroxyl ions are fairly reproducible. As a matter of fact, the aluminum electrode does not function as a pH electrode but it does as a pOH electrode in the presence of an excess of hydroxyl ions. In acid media containing fluoride the depolarization potential is fairly reproducible and found to vary with pH and fluoride concentration. However, when exact information concerning the change in pH during a potentiometric titration is desired, the aluminum electrode, even in the presence of a trace of fluoride, cannot be recommended as a substitute for the host of readily available and more precise pH-indicator electrodes.

We have made an extensive study of the voltammetric properties of a rotated aluminum wire electrode in various supporting electrolytes. Of all ions tested only hydroxyl and fluoride ions were found to depolarize the electrode anodically at very high negative potentials. Use of this fact is made in a rapid amperometric method for the determination of fluoride in solution and in the amperometric titration of fluoride with a suitable cation, to be described in subsequent papers.

The main characteristic of the current–potential curves (voltammograms) in the absence of depolarizing hydroxyl and fluoride ions, is that the electrode remains highly polarized over a wide range of potentials both in the presence and absence of oxygen. This means that the electrode potential is ill-defined and hard to reproduce. In connection with the voltammetric studies potentials were measured in different media of varying pH and the results are described and discussed in the present paper.

EXPERIMENTAL

Materials

Pure aluminum wire. Aluminum rod, 1/16 inch diameter was prepared for us by the Aluminum Company of America and we like to express our sincere appreciation to this company for this courtesy. The reported analysis stated that the sample was composed of: Al, 99.99%; Cu, 0.001%; Si, 0.001%; Zn, 0.005%; others, 0.000%. Conductivity water and reagent chemicals were used in all experiments. In registering current–potential curves in the absence of oxygen an inert atmosphere was maintained by passing 99.99% pure nitrogen obtained from Linde Air Products Co.

Instrumentation.

Current–potential curves were recorded with a Leeds and Northrup Electrochemograph. For the measurements of current at a given potential both the polarograph and a manual apparatus were used. Potentiometric readings were taken with a Leeds and Northrup Student potentiometer. All experiments were carried out at 25°. The pH of all buffered and unbuffered solutions was measured with a Beckman glass electrode pH meter, after the equilibrium potential of the aluminum electrode had been measured. Determinations were carried out in a 100-ml cell equipped with an inlet tube for the introduction of nitrogen which was passed through the solution until it was oxygen-free and then over the solution during the recording of voltammograms. Connection to the saturated calomel electrode was made with a sodium nitrate salt bridge to prevent diffusion of chloride ions into the solution. Unless otherwise stated, the measurements were run from positive to negative potentials. Reported potentials refer to the S.C.E.

Construction of electrode

Considerable difficulty was encountered in constructing a satisfactory rotating aluminum electrode, hereafter designated as R.Al.E. The model depicted in Fig. 1 has been found suitable. It has been prepared in the following way: a straight piece of pure aluminum rod (10 cm long, 1.5 mm outside diameter) was attached by means of a screw joint to a short piece of stainless steel rod (2 cm long, 3 mm outside diameter). This assembly was introduced into two glass tubes, the upper part of which was 8 cm long and 0.6 cm wide, with a bore size of 0.5 cm, while the lower one was an equally wide tube, 9.4 cm in length but only 0.2 cm in bore size. The top tube contained only the stainless steel rod whereas the aluminum wire was contained in the narrow tube except that 0.6 cm protruded from the end. With the aid of a non-conducting film of adhesive cement the electrode was cemented to the bottom of the narrow tube leaving about 0.5 cm of aluminum exposed to the environment. This uncovered part of the wire served as electrode. The cement coating proved to be effective in insulating and very durable. A thin layer of apiezon W wax may also be used in place of the cement. To avoid any possibility of contact between mercury and the aluminum, a thick layer of apiezon W wax was placed and melted into the upper tube covering half of the stainless steel rod. The rest of the tube was filled with mercury to make electrical connection. The electrode was rotated at 600 r.p.m. by means of a Sargent synchronous motor.

Pretreatment of the R.Al.E.

The electrode was initally polished with emery paper, then it was kept in concentrated nitric acid for 30 min and thoroughly washed with distilled water before use. The same electrode was employed throughout all the experiments. Later a new electrode was constructed and its behavior was found to be closely similar to that of the first electrode. Great difficulties were experienced in reproducing current–potential curves. Their shapes and the zero current potentials were found to vary greatly with the pretreatment of the electrode, after a run had been made. The following types of treatment did not improve the reproducibility: cleaning with sand paper followed by anodic and cathodic polarization in acetate buffer pH = 3 at 1 V *versus* S.C.E. for 1 min pretreatment in concentrated nitric acid followed by the same polarization; cleaning in 0.1*M* sodium hydroxide in the absence or presence of 0.3*M* cyanide as recommended by SCARANO[3]; this treatment supposedly dissolves a film of oxide; cleaning in 0.05*M* sodium fluoride. Finally it appeared that the most reproducible results were obtained by keeping the electrode for about 20 min in a 0.02*M* solution of ethylenediaminetetraacetate in 0.2*M* acetic acid, pH 3, followed by anodic and cathodic polarization for 1 min at 1 V *versus* S.C.E. in this medium.

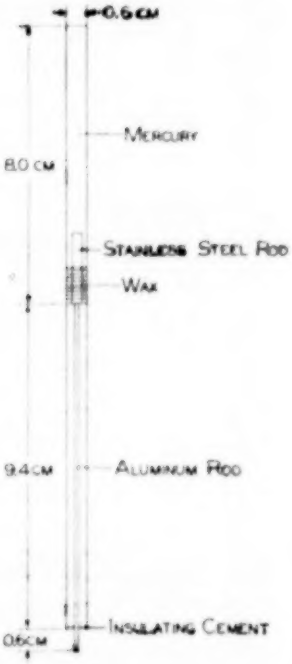

Fig. 1. The rotated aluminum electrode.

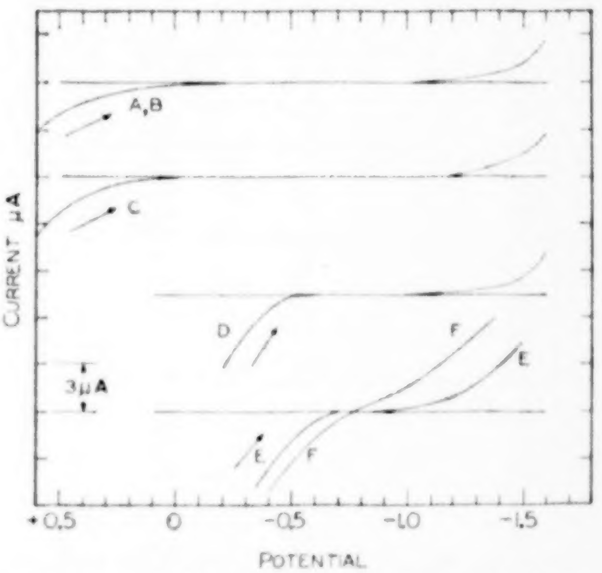

Fig. 2. Voltammograms measured from positive to negative potentials in oxygen-free solutions of: A, 0.2*M* HAc; B, 0.01*M* $NaNO_3$; C, 0.017*M* sodium benzoate; D, 0.01*M* $NaClO_4$; E, 0.01*M* $HClO_4$; F, 0.1*M* $HClO_4$.

Current–potential curves

The shapes of current–potential curves measured in various supporting electrolytes are shown in Figs. 2, 3 and 4. Each curve shown in Fig. 2 was recorded automatically from positive to negative potentials starting at +0.6 V *versus* S.C.E. with a scanning rate of 3.3 mV per second. Before each run the R.Al.E. was cleaned by the recommended procedure.

Voltammograms in Figs. 3 and 4 were run from positive to negative potentials and then in the reverse direction starting at −1.5 V. The electrode was then cleaned before placing in another electrolyte solution. The general shape of the curves in Fig. 3 is the same whether run from positive to negative or negative to positive potentials. In supporting electrolytes composed of an acetate buffer alone or with nitrate (Fig. 2), benzoate, phosphate (Fig. 3), sulfate or EDTA the electrode is strongly polarized from about +0.6 to −1.4 V, and the electrode potential (zero current–potential) is poorly defined and difficult to reproduce.

From Fig. 4 it is seen that perchlorate, chloride and bromide depolarize the electrode anodically. When the curves are run from positive to negative potentials, the anodic depolarization starts near −0.6 V, but at less negative potentials when run from negative to positive potentials. Under the latter conditions the lines representing the anodic currents are more drawn out. The values of the depolarization potentials also change with concentration of depolarizing anions. Voltammograms were also run in air-saturated solutions. In all instances the curves had the same appearance as in oxygen-free solutions, except that in the same electrolyte solution the potential was about 0.15 V less negative in the presence than in the absence of oxygen. Evidently, oxygen does not depolarize the electrode cathodically.

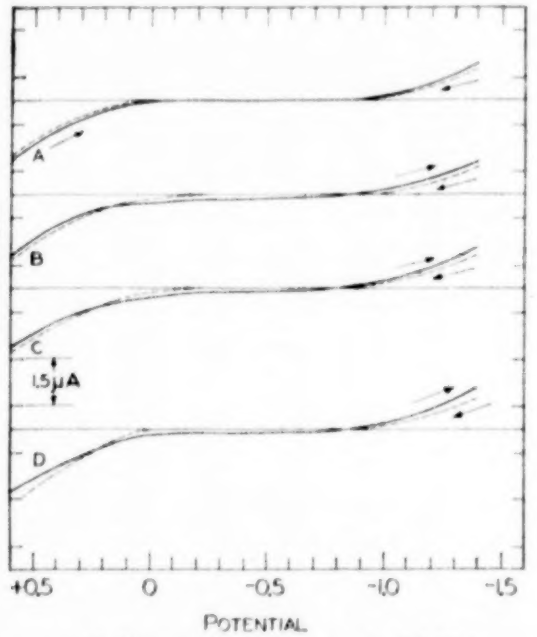

Fig. 3. Voltammograms in 0.2*M* HAc + 0.05*M* NaAc, pH = 4.0. A, no addition; B, 0.01*M* in Na_2SO_4; C, 0.01*M* in $NaNO_3$; D, 0.01*M* in $NaH_2PO_4 \cdot H_2O$. Dotted lines, potential changed from − to + values.

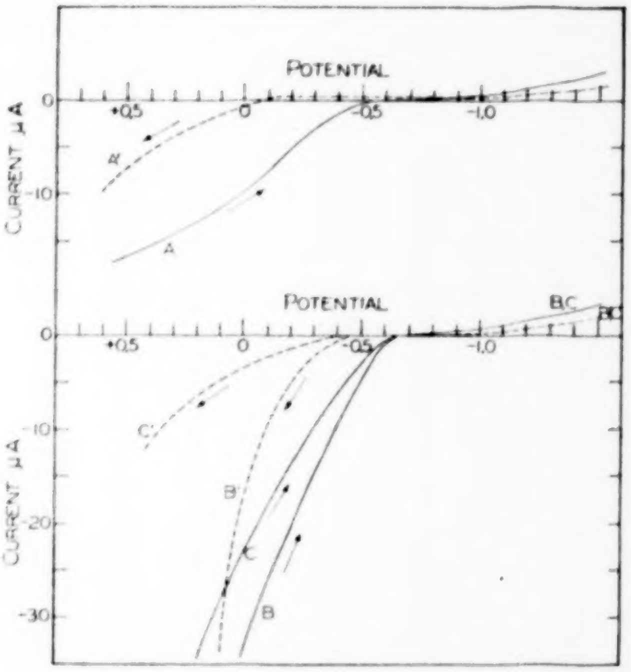

Fig. 4. Effect of chloride, bromide and perchlorate in acetate buffer (pH = 4.0). A, 0.01*M* in $NaClO_4$; B, 0.01*M* in NaCl; C, 0.01*M* in NaBr. Dotted lines, potential changed from − to + values. Curves A, B, and C were run after applying +0.6 V during 5 min before running, while curves A′, B′ and C′ were run after polarizing for 5 min at −1.5 V.

No detailed systematic study has been made in order to interpret the above observations. It appears that the electrode is covered with a film of oxide, even after cleaning in the EDTA-containing buffer. This is substantiated by the fact that anodization at +1 V after cleaning had no effect on the shape of the various current–potential curves. The depolarization by perchlorate, chloride and bromide ions might be attributed to a limited permeability of the film for these ions. Phosphate reacts with aluminum ions to form a slightly soluble compound, while EDTA forms a fairly stable complex with aluminum. Still, these ions do not depolarize anodically the aluminum electrode, which is accounted for by the assumption that the film is impervious to these ions. Similarly, the film seems to be impervious to oxygen.

Hydroxyl and fluoride ions depolarize the electrode and it is concluded that the film is permeable to these ions. As an example, voltammograms of fluoride are given on 0.2*M* acetic acid and in 0.01*M* perchloric acid (Fig. 5). A diffusion current region is obtained and use of this can be made in the amperometric determination of fluoride in very dilute solutions. This will be discussed in more detail in a subsequent paper. Also the potential of the electrode is better defined in fluoride-containing solutions. This is evident from the fairly steep slope of the current–potential curve near the zero current potential.

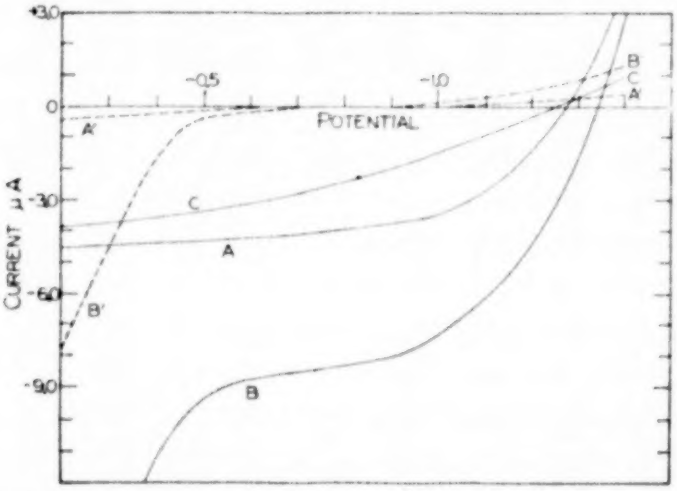

Fig. 5. Depolarization of the R.Al.E. by fluoride in various media. A, $4 \cdot 10^{-5}M$ NaF in 0.2*M* HAc; B, $7 \cdot 10^{-5}M$ NaF in 0.01*M* $HClO_4$; C, $4 \cdot 10^{-5}M$ NaF in 0.2*M* HAc after anodizing electrode for 2 h at 1 V. Dotted lines, A′, B′ are the residual currents in the supporting electrolytes alone.

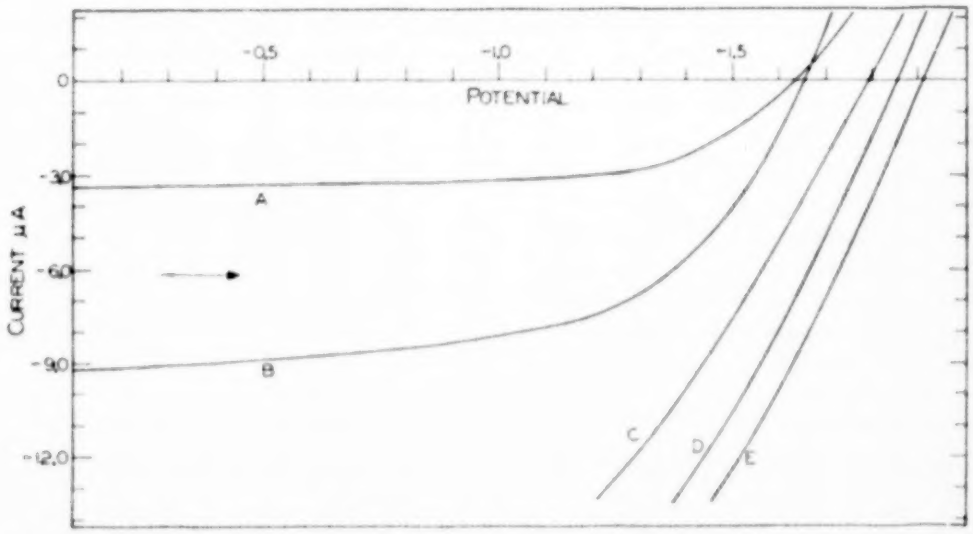

Fig. 6. Depolarization of electrode in alkaline medium. Voltammograms in air-free mixtures of 0.01*M* $NaNO_3$ and NaOH. Concentration of NaOH: A, $1 \cdot 10^{-4}M$; B, $2.6 \cdot 10^{-4}M$; C, $1.1 \cdot 10^{-3}M$; D, 0.01*M*; E, 0.1*M*.

After cleaning, the electrode was anodized in 0.2*M* acetic acid–0.02*M* sodium acetate at +1 Volt for 2 h. Although the current was small, a film on the electrode was visible to the naked eye. This electrode was then placed in a $4 \cdot 10^{-5}M$ fluoride solution in 0.2*M* acetic acid and a voltammogram run (Fig. 5, curve C). Again a diffusion current region is observed, but the curve is much more drawn out than curve A, indicating that the heavier film on the electrode after anodizing exerts an interfering effect on the depolarization by fluoride, but is still permeable to fluoride ions.

Hydroxyl ions, like fluoride ions, depolarize the electrode anodically. Some typical voltammograms in sodium hydroxide solutions of varying strength are shown in Fig. 6. In dilute hydroxide solutions typical well defined diffusion current regions are observed (Fig. 6). Also, from the slopes of the curves at the zero current potential it is apparent that the electrode potential is fairly well defined in the presence of an excess of hydroxyl ions. Dilute solutions of sodium carbonate yield current–potential curves similar to those observed in dilute sodium hydroxide solutions.

Potential measurements

Potentials of the R.Al.E. in solutions of pH values ranging from 1.1 to 13 were determined in the presence and absence of air. The electrode was first cleaned in the EDTA solution and potentials were measured in the various solutions in the order from pH 1 to pH 7. After a constant potential had been attained, the electrode was rinsed with distilled water before the next measurement. After the measurement in the solution of pH 7 the electrode was cleaned in EDTA and potentials were measured in alkaline solutions in the order from pH 13 to pH 9. Potential readings were made at 2 min intervals and the electrode was considered to have attained the stationary potential when the reading did not change in a 5 min period. The pH was measured after the equilibrium potential had been determined. Results are shown in Table I. In acid medium ($0.1M$ perchloric acid, $0.1M$ hydrochloric acid, $0.1M$ acetic acid, $0.1M$ acetic acid–$0.1M$ sodium acetate) potential readings were irregular and reproducibility was very poor. The reported values are average potentials. Dependent on the previous history of the electrode, the potential was found to fluctuate in acid medium between −0.6 and −0.9V (*vs.* S.C.E.). Time required to attain stationary values varied from 10 to 82 min in these media. Once the stationary potential had been attained a change of pH in the solution did not affect the potential, indicating that the electrode does not function as a pH electrode in acid media. In acid air-saturated solutions the initial potentials were about 0.2 V more positive than in the absence of air, but the poorly defined stationary potentials slowly approached the same values. In oxygen-free alkaline solutions with a pH greater than 10 the equi-

TABLE I

POTENTIALS (IN V *vs.* S.C.E.) IN SOLUTIONS OF VARIOUS pH IN THE ABSENCE OF AIR

Electrolyte	*pH*	$-E$
$0.1M$ $HClO_4$	1.10	0.6–0.8
$0.1M$ HAc	2.87	0.6–0.8
$0.1M$ HAc–$0.1M$ NaAc	4.62	0.6–0.9
$0.1M$ $NaNO_3$	6.9	0.8–0.9
$0.1M$ Borax	9.2	1.576
$0.05M$ Na_2CO_3 + $0.05M$ $NaHCO_3$	10.0	1.692
$0.001M$ Borax + $0.05M$ Na_2CO_3	11.0	1.776
$0.01M$ NaOH	(12.2)[a]	1.845
$0.1M$ NaOH	(13.2)[a]	1.912
$1M$ NaOH	(14.2)[a]	1.975

[a] not measured.

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librium potential was established almost instantaneously and the potential was reproducible within 5 mV. Oxygen affects the potential of the electrode in alkaline solutions making it less negative. For example, the stationary potential of 0.1*M* borax in nitrogen was —1.576 V but in oxygen saturated solution —1.340 V. In 0.01*N* sodium hydroxide the values were —1.847 and —1.676 V respectively. The oxygen effect will be discussed further in a subsequent paper.

In the pH range between 11 and 14 the potential of oxygen-free solutions was found to change as an average 66 mV per unit change in pH. Assuming that the reaction.

$$\mathrm{Al} + 4\mathrm{OH}^- \rightleftharpoons \mathrm{H_2AlO_3}^- + \mathrm{H_2O} + 3e$$

is reversible and that the system remains saturated to the oxide, a standard potential ($[\mathrm{OH}^-] = 1$) of —1.97 V (*vs.* S.C.E.) is calculated from the data in Table I. LATIMER[1] calculated a value of —2.31 V (*vs.* N.H.E.) or —2.55 V (*vs.* S.C.E.). Our value is about 0.6 V less negative than the calculated figure, but it is in good agreement with PLUMB's data[4].

As mentioned in the previous section, fluoride ions depolarize the electrode in acid media. As it is evident from the data in Table II, even a trace of fluoride ($2 \cdot 10^{-5} M$ has a profound effect on the potential of the aluminum electrode. Potentials are of the order of 300 to 600 mV more negative than in the absence of fluoride and they are reproducible within 10 mV. Oxygen shifts the potential to less negative values. In acid medium the potential changes only about 10 mV per unit change in pH, while at a pH greater than 10 the potentials are practically the same as those in the absence of a trace of fluoride. A more detailed account of the effect of the concentration of fluoride upon the electrode potential will be given in a subsequent paper in connection with a discussion of the potentiometric determination and titration of fluoride.

TABLE II

POTENTIALS (IN V *vs.* S.C.E.) IN SOLUTIONS CONTAINING $2 \cdot 10^{-5} M$ FLUORIDE

Electrolyte	*pH*	$-E$
0.1 *M* $\mathrm{HClO_4}$	1.2	1.236
0.01 *M* $\mathrm{HClO_4}$	2.1	1.247
0.1 *M* HAc	2.9	1.253
0.1 *M* HAc–0.1 *M* NaAc	4.62	1.271
0.1 *M* NaAc	8.2	1.543
0.01 *M* NaOH		1.847
0.1 *M* NaOH		1.912

From the present study it is evident that the aluminum electrode functions as a hydroxyl ion indicator electrode at a pH greater than 9 and as a fluoride ion indicator electrode in acid medium.

ACKNOWLEDGEMENT

Acknowledgement is made to the Graduate School of the University of Minnesota for financial support of this research.

SUMMARY

A rotated aluminum wire electrode (R.Al.E.) is described for the determination of voltammograms and potentials. An aluminum electrode is highly polarizable both cathodically and anodically. Of all ions tested only hydroxyl and fluoride ions depolarize it anodically at highly negative potentials. In the absence of fluoride it is not a pH electrode, but it is a pOH electrode in the presence of an excess of hydroxyl ions. Fluoride in acid medium and hydroxyl ions yield well defined anodic diffusion currents. In the absence of fluoride or of an excess of hydroxyl ions the potential is ill defined. In acid medium a trace of fluoride ($2\cdot10^{-5}M$ or 0.4 p.p.m.) causes the potential to become approximately 600 mV more negative than in the absence of fluoride. At a pH greater than 11 the potential varies 66 mV per unit change of pH.

RÉSUMÉ

Une électrode tournante d'aluminium est décrite pour la détermination de ,,voltammogrammes" et de potentiels. Une électrode d'aluminium est très polarisable soit cathodiquement, soit anodiquement. De tous les ions essayés, seuls les ions hydroxyles et fluorures la dépolarisent anodiquement à des potentiels fortement négatifs. C'est une électrode de pOH en présence d'un excès d'ions OH^-. Les fluorures, en milieu acide et les ions hydroxyles donnent des courants de diffusion anodiques bien définis. En l'absence de fluorure ou d'un excès d'ions hydroxyles, le potentiel est mal défini.

ZUSAMMENFASSUNG

Es wird eine rotierende Elektrode aus Aluminium für die Bestimmung von ,,Voltagramme" und Potentialen beschrieben. Eine Aluminiumelektrode ist sowohl anodisch als auch kathodisch stark polarisierbar. Von allen untersuchten Ionen wird sie nur durch OH-Ionen und Fluorid-Ionen anodisch depolarisiert bei stark negativem Potential. Sie wirkt als pOH Elektrode in Gegenwart eines Überschusses von OH-Ionen. Fluoride in saurem Milieu und OH-Ionen geben gut definierte anodische Diffusionsströme. Bei Abwesenheit von Fluorid oder wenn zu wenig OH-Ionen zugegen sind, ist das Potential nicht eindeutig.

REFERENCES

[1] W. M. Latimer, *Oxidation Potentials*, Prentice-Hall, Inc., New York, 1952.
[2] J. Heyrovsky, *J. Chem. Soc.*, 117 (1920) 35.
[3] E. Scarano, *Anal. Chim. Acta*, 16 (1957) 365.
[4] R. C. Plumb, Effect of the oxide film at the aluminum electrode, *J. Electrochem. Soc.*, in the press.

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SOLVENT EXTRACTION OF ANTIMONY(V) WITH ETHYL ACETATE

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In the course of an investigation on metal antimonates, it was found that by extraction with ethyl acetate, moderate amounts of antimony (V) could be quantitatively separated from Pb(II), Sn(IV), Ni(II), Cr(III) and Hg(II) in 6 *N* HCl. Extraction of antimony(V) either as the rhodamine-B chlorantimonate[1] or the citrate–oxalate complex[2] with ethyl acetate has been reported; these methods, however, are limited to trace determinations. The proposed method is applicable for the extraction of moderate amounts (0.05 to 0.2) of antimony(V) and is much simpler and more rapid. Lead(II), tin(IV), mercury(II), nickel(II) and chromium(III) are non-interfering. Moderate amounts of copper(II) similarly have no effect; but iron(III), tin(II), cadmium(II) and cobalt(II) are co-extracted and must be removed. The method has been successfully used for the determination of antimony in Pb, Sn, Ni, and/or Hg antimonates and for the analysis of type metal.

REAGENTS

Antimony stock solution

Approximately 32 ml of $SbCl_5$ (B.D.H. reagent grade) was dissolved in 250 ml of standard 6 *M* HCl. The solution was filtered through glass wool to remove suspended impurities and stored in a closed bottle provided with a semi-micro delivery burette. Definite volumes of the solution were removed and their antimony content determined iodometrically[3].

Hydrochloric acid stock solution

AnalaR HCl was diluted to 6 *M* and accurately standardized.

Ethyl acetate

Reagent grade, redistilled.

Standard decinormal thiosulphate solution

AnalaR sodium thiosulphate was dissolved in distilled water to make a *N*/10 solution. It was standardized against AnalaR potassium dichromate.

Other salts used were either B.D.H. AnalaR grade or Mercks pure reagents.

PRELIMINARY INVESTIGATION

Before attempting the actual separation of antimony from interfering elements, the effects of HCl concentration and Sb concentration on the extraction were examined. Preliminary extractions were carried out with a 1.0 *M* $SbCl_5$ solution in conc. (11.6 *N*) HCl. It was observed that extraction does not substantially increase above 6 *N* HCl, but when extractions were carried out with solutions more concentrated than 6 *M* in HCl, considerable reduction in volume of the ethyl acetate layer occurs. The volume reduction was nearly 50% with 8 *N* HCl, 60% with 10 *N* HCl and with 11.6 *N* HCl, no separation of the two layers were observed. Difficulties were also encountered in maintaining constant acidities of these solutions. Therefore, for the subsequent study a solution of $SbCl_5$ (1.0 *M* app.) in 6 *N* HCl was used.

EXPERIMENTAL PROCEDURE

The experimental solutions used for extraction were prepared by mixing together varying amounts of the antimony(V) stock solution, standard 6 *N* HCl and distilled water. The total volume was always 10 ml and contained known amounts of antimony(V) in the presence of varying amounts of HCl. The HCl content was calculated by assuming the antimony(V) stock solution to be 6 *M* in HCl. These solutions were extracted with an equal volume of ethyl acetate in a graduated syringe extractor[4] for 1 min. On the separation of the two layers, the phase volume was read and the organic layer removed. This was treated with 25 ml HCl and kept for some time until a homogenous phase resulted upon the addition of water. This solution was analysed for antimony by the iodometric method[3].

RESULTS AND DISCUSSION

Effect of HCl concentration

The effects of varying the HCl concentration on the extraction are given in Table I. It is immediately clear that high acidity is essential for satisfactory extraction. With solutions lower than 3.0 *M* in HCl, antimony(V) immediately hydrolyses and after shaking with ethyl acetate it is difficult to separate the two layers; the extent of extraction is, in addition, quite low (less than 30%) although, there is no appreciable reduction in the volume of the solvent. With stronger acid solutions, no hydrolysis occurs and the extraction continuously increases; however, there is a reduction in the volume of the solvent. As has been previously pointed out, higher acidities do not improve the extraction in any way. 6 *N* HCl solutions appeared to be most suitable since the extraction is considerable (87%) and the reduction in the volume of the solvent is little.

TABLE I

EXTRACTIBILITY OF ANTIMONY(V) BY ETHYL ACETATE AS INFLUENCED BY THE STRENGTH OF HCl

Antimony taken for each extraction 0.1128 g

Molarity of HCl	*Final volume of organic layer ml*	*Percentage extraction*
6.00	8.0	87.48
5.97	8.0	86.42
5.97	8.0	85.88
5.97	8.0	86.96
5.82	8.0	84.82
5.82	8.0	85.35
5.73	8.0	84.03
5.73	8.0	84.82
5.67	8.0	83.75
5.67	8.0	84.82
5.37	8.0	80.02
5.37	8.0	81.65
5.08	8.0	81.70
5.08	8.0	81.65
4.78	8.0	71.22
4.78	8.0	68.28
4.18	8.5	53.34
4.18	8.5	54.68
3.58	9.0	36.00
3.58	9.0	42.68
2.99	9.5	27.20[a]
2.69	9.5	28.80[a]
2.39	10.0	26.68[a]
2.09	10.0	29.34[a]

[a] Hydrolysis takes place

Effect of antimony(V) concentration

The effect of antimony(V) concentration on extraction was subsequently examined. Keeping the acidity (HCl) and volume of the solution identical with that found optimum in previous experiments, only the antimony content was varied between such limits as appeared suitable for rapid and accurate volumetric estimation. Results are given in Table II. It will be noted that a four-fold change in metal concentration produces but little effect. A slight improvement in extraction is noted with increasing antimony concentration.

Distribution coefficient of Sb(V) under optimum conditions

The distribution coefficient of antimony under optimum conditions was next determined by extracting 5, 10 and 15-ml portions of solutions containing (1.0007 g) Sb(V) in 6 *N* HCl. The average value corresponds to 6.56 at 25–28°. It is obvious that 3 extractions will quantitatively separate the antimony(V).

TABLE II

PERCENTAGE EXTRACTION WITH DIFFERENT AMOUNTS OF ANTIMONY

Antimony taken g	*Percentage extractions*
0.0564	85.63
0.1128	87.48
0.1692	88.51
0.2256	91.47

Behaviour of other interfering ions

Under optimum conditions, iron(III) is completely co-extracted while tin(II), cadmium(II) and cobalt(II) are moderately extracted. Moderate amounts (0.0167 to 0.05 g) of copper(II) have no effect but larger amounts introduce a positive error.

TABLE III

RESULTS FOR ANTIMONY(V) IN THE PRESENCE OF INTERFERING ELEMENTS

Element	*Amount added* g	*Added as*	*Antimony taken* g	*Antimony found* g	*Difference* %
Nickel	0.05	$NiSO_4 \cdot 7\ H_2O$	0.1007	0.1007	0.0
	0.10	,,	0.1007	0.1001	—0.6
	0.15	,,	0.1007	0.1007	0.0
Chromium	0.05	$CrK(SO_4)_2 \cdot 12\ H_2O$	0.1007	0.1007	0.0
	0.10	,,	0.1007	0.1001	—0.6
	0.15	,,	0.1007	0.1001	—0.6
Lead	0.10	$Pb(OOCCH_3)_2 \cdot 3\ H_2O$	0.1007	0.1001	—0.6
	0.90	,,	0.1007	0.0999	—0.8
Tin	0.05	$SnCl_2 \cdot 2\ H_2O$, oxidized with $KClO_3$	0.1013	0.1007	—0.6
	0.10	,,	0.1013	0.1013	0.0
	0.15	,,	0.1013	0.1013	0.0
Copper	0.0167	$CuSO_4 \cdot 5\ H_2O$	0.1013	0.1007	—0.6
	0.0333	,,	0.1013	0.1019	+0.6
	0.0500	,,	0.1013	0.1019	+0.6
	0.1000	,,	0.1013	0.1030	+1.7
	0.1500	,,	0.1013	0.1061	+4.8
Mercury	0.05	$HgCl_2$	0.1037	0.1024	—1.3
	0.10	,,	0.1037	0.1042	+0.5
	0.15	,,	0.1037	0.1042	+0.5
Tin and lead	0.10 g Sn(IV)	$SnCl_2 \cdot 2\ H_2O$ oxidized with $KClO_3$	0.1007	0.1006	—0.1
and	0.90 g Pb(II)	$Pb(OOCCH_3)_2 \cdot 3\ H_2O$			
Type metal[a]			0.1400	0.1403	+0.3

[a] Type metal containing 14% Sb, 81% Pb, 5% Sn.

Determination of antimony in the presence of other elements

Determination of antimony in synthetic mixtures with other elements was carried out by 3 extractions with ethyl acetate from 6 *N* HCl. Results are given in Table III and indicate that the method is quite suitable for the rapid determination of antimony(V) in the presence of Pb(II), Sn(IV), Ni(II), Cr(III) and Hg(II). Maximum deviation is within ± 1%.

RECOMMENDED PROCEDURE FOR ANTIMONATES AND TYPE METAL

Method for antimonates

Decompose 0.25 g of antimonate with 15 ml conc. HCl in a casserole. Boil down to 5 ml, add 5 ml conc. HCl, and after cooling, dilute with an equal volume (10 ml) of distilled water. Transfer the clear solution to a syringe extractor. Wash the casserole with 20 ml of ethyl acetate and draw the solvent into the extractor. Extract for 1 minute, allow for separation and remove the solvent layer. Add 20 ml of fresh ethyl acetate to the casserole and draw again into the extractor. Repeat the extraction once more (3 times in all). Treat the combined extracts with 25–30 ml conc. HCl and heat gently until a homogeneous solution results up on the addition of water. Dilute to 20% v/v HCl with water. Add 2–3 g KI and titrate the liberated iodine with standard *N*/10 thiosulphate in the usual way.

Method for type metal

Treat 1 g of type metal with 20 ml conc. HCl containing 2 ml bromine (liquid). Towards the end of the reaction heat gently until solution is complete. Add 10 ml of 20 vol. hydrogen peroxide and boil to completely remove bromine. Evaporate to near dryness and add 10 ml of conc. HCl. After cooling, dilute with 10 ml of distilled water. Subject the solution to extraction with ethyl acetate in the same fashion as given above for antimonates.

SUMMARY

A method has been derived for the selective extraction of antimony(V) from hydrochloric acid solution with ethyl acetate. The method can be employed for the rapid determination of antimony in antimonates of lead, tin, mercury, nickel and chromium and in type metal. Iron(III), cobalt(II) cadmium(II), and large amounts of copper(II) and tin(II) interfere with the extraction. For the analysis of type metal, tin must be oxidized to the tetravalent state.

RÉSUMÉ

Une méthode est proposée pour l'extraction sélective de l'antimoine(V), en solution chlorhydrique, au moyen d'acétate d'éthyle. Ce procédé permet un dosage rapide de l'antimoine en présence de plomb, d'étain(IV), de mercure, de nickel et de chrome. Par contre, le fer(III), le cobalt, le cadmium et de grandes quantités de cuivre et d'étain(II) gênent.

ZUSAMMENFASSUNG

Antimon lässt sich aus salzsaurer Lösung mit Aethylacetat selektiv extrahieren. Diese Methode erlaubt eine rasche Bestimmung von Antimon neben Blei, Zinn-(4), Quecksilber, Nickel und Chrom. Störend wirken Eisen-(3), Kobalt, Cadmium sowie grössere Mengen von Kupfer und Zinn-(2).

REFERENCES

[1] G. H. MORRISON AND H. FREISER, *Solvent Extraction in Analytical Chemistry*. John Wiley, New York, 1957, p. 154.

[2] C. E. WHITE AND H. J. ROSE, *Anal. Chem.*, 25 (1953) 351.

[3] N. H. FURMAN, ed. *Scott's Standard Methods of Chemical Analysis*, 5th ed., Vol. I, Van Nostrand, New York, 1939, p. 75.

[4] A. I. MEDALIA AND R. W. STOENNER, *Anal. Chem.*, 23 (1951) 545.

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HIGH FREQUENCY TITRATION AND ESTIMATION OF IONS

II. DETERMINATION OF BARIUM, LEAD, THALLIUM, CALCIUM, CERIUM, COPPER AND SILVER

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Recently MAJUMDAR AND MUKHERJEE[1] have estimated silver volumetrically with various organic and inorganic reagents using high frequency titrimetry. The utility of this technique has been widely illustrated by the authors in the present paper. A number of different metal ions has been estimated with standard solutions of chromate, oxalate and ferrocyanide and the accuracy has been found to be no less than that obtained with classical gravimetric or volumetric methods. The only difficulty observed is that with high ionic concentration, the end-point is not sharp enough, due perhaps to the low frequency of the crystal (6 Mc) used in the instrument.

The high frequency technique is only a special form of conductometry. However, absence of contact between the electrodes and the solution eliminates errors caused by coating of the electrodes by a precipitate and other surface phenomenon. The general applicability of the high frequency method to precipitation titrations[2-4] suggests an investigation of the new volumetric technique for the determination of elements using a high frequency oscillator for end-point detection.

EXPERIMENTAL

Apparatus and chemicals

The apparatus used is identical with that reported in a previous paper[1].

The chemicals and the reagents used were all of A.R. quality.

Lead, barium and thallium(I) were estimated with standard potassium chromate solution.

Although a number of methods have been developed for their determinations, the number of good volumetric procedures is limited. The ordinary methods for the determination of these elements involve precipitation by chromate solution and determination of the iodine evolved on their reaction with potassium iodide. KOLTHOFF AND PAN[5] have described an amperometric method for the determination of lead with dichromate as the titrant. High frequency titration of these elements by chromate is greatly simplified and the time required for each titration is much less than the ordinary volumetric procedure.

Procedure

A measured volume of the solution to be analysed was taken in the titration cell which consisted of a 100-ml beaker with two metal rings on its outside surface. Since about 70 ml of the solutions were required to cover the rings, all titrations were carried out with this amount as the initial volume. The solution, after dilution to the required volume, was titrated with the standard solution of chromate, after the high frequency instrument was tuned to resonance (maximum power absorption by the cell solution) with the tuning condenser. The course of the titration is followed exactly in the same manner as previously reported[1]. The titration curves, obtained by plotting the change in dial reading per volume increment of the titrant, against the volume of the titrant, are shown in Fig. 1.

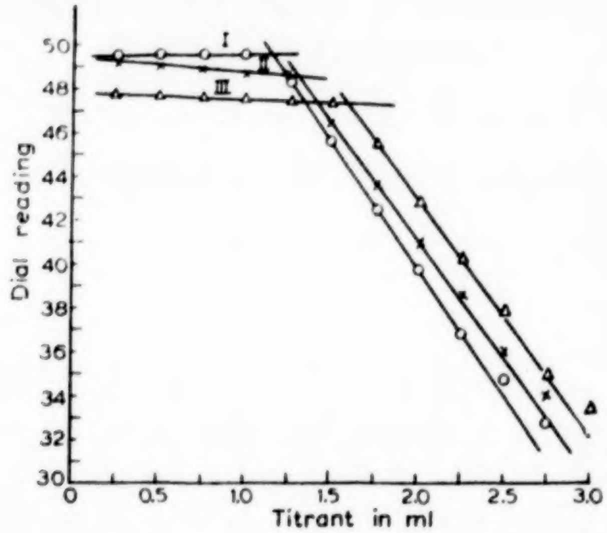

Fig. 1. I. Titration of $1.71 \cdot 10^{-2} M$ Pb^{+2} by $3.534 \cdot 10^{-2} M$ K_2CrO_4.
II. Titration of $1.851 \cdot 10^{-2} M$ Ba^{+2} by $3.530 \cdot 10^{-2} M$ K_2CrO_4.
III. Titration of $2.291 \cdot 10^{-2} M$ Tl^{+} by $3.534 \cdot 10^{-2} M$ K_2CrO_4.

The results of analysis are presented in Table I. An accuracy of about $\pm 1\%$ was observed for the majority of the cases. In the case of lead, the pH of the solution was kept between 5.0 to 6.5, and at this pH, lead up to 20 mg was estimated. For barium, the pH of the solution was kept between 6.0 to 6.5 when up to 20 mg of the metal was determined. Presence of calcium and magnesium, up to a maximum concentration of 5 mg (Ba, 10 mg), does not interfere. Thallium(I), when present up to a maximum concentration of 50 mg, was estimated at a pH between 6–6.5.

TABLE I

	Metal taken mg	*Found mg*	*Deviation*
Pb	3.54	3.51	−0.03
	8.86	8.79	−0.07
	17.72	17.73	+0.01
Ba	6.35	6.30	−0.05
	12.70	12.60	−0.10
	19.0	18.9	−0.10
Tl	4.68	4.64	−0.04
	23.41	23.20	−0.21
	46.82	46.44	−0.38

Estimation of calcium and cerium by ammonium oxalate

Calcium and cerium(III) were determined by direct titration with a standard solution of ammonium oxalate in presence of 30% (v/v) of ethyl alcohol. In the absence of alcohol, precipitation of calcium and cerium oxalates was found to be slow and hence the detection of their end-points was rather difficult.

By this method, calcium up to 10 mg was estimated at a pH near 5.5. Accurate determination of Ce(III) by oxalate was possible only when the cerium content was between 10 and 40 mg. At lower concentrations, errors were high probably due to the slow coagulation of the precipitate. Ce(III), if present in very small amounts, could be estimated by adding to it a known excess and then titrating; the actual cerium content was then found by difference. Results are shown in Table II (Fig. 2).

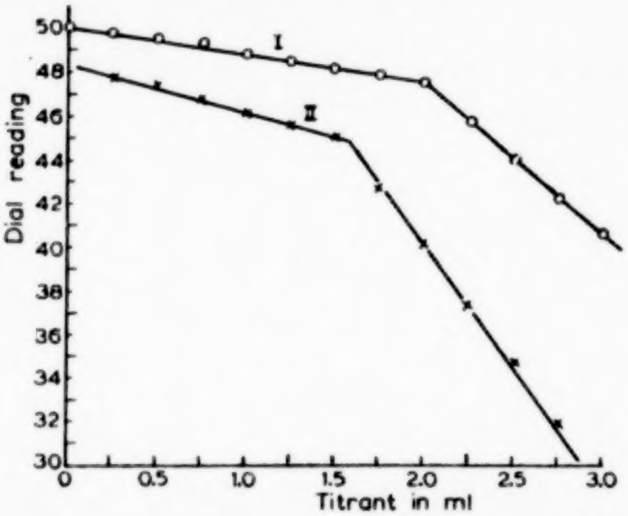

Fig. 2. I. Titration of $4.021 \cdot 10^{-2} M$ Ca^{+2} by $5.00 \cdot 10^{-2} M$ $(NH_4)_2C_2O_4$. II. Titration of $2.565 \cdot 10^{-2} M$ Ce^{+3} by $6.819 \cdot 10^{-2} M$ $(NH_4)_2C_2O_4$.

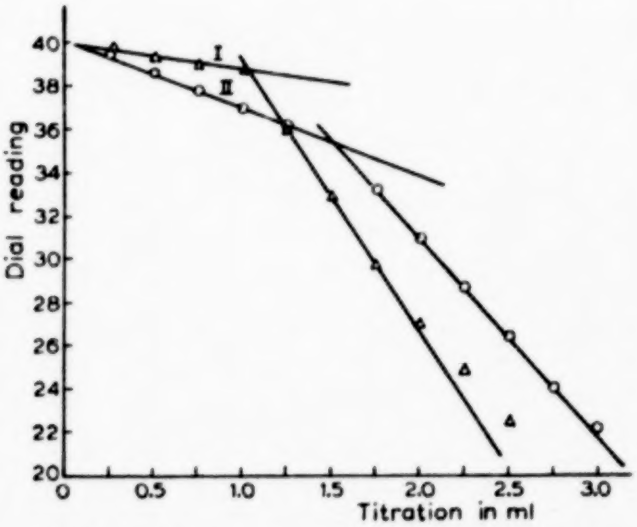

Fig. 3. I. Titration of $1.697 \cdot 10^{-2} M$ Ag^+ by $2.015 \cdot 10^{-2} M$ $K_4Fe(CN)_6$. II. Titration of $2.447 \cdot 10^{-2} M$ Cu^{+2} by $2.16 \cdot 10^{-2} M$ $K_4Fe(CN)_6$.

TABLE II

Metal taken *mg*		*Found* *mg*	*Deviation*
Ca	4.02	4.00	—0.02
	8.04	8.01	—0.03
Ce	10.26	10.20	—0.06
	20.52	20.48	—0.04
	41.04	40.84	—0.20

TABLE III

Metal taken *mg*		*Found* *mg*	*Deviation*
Cu	3.88	3.84	—0.04
	7.76	7.70	—0.06
Ag	9.15	9.12	—0.03
	18.30	18.25	—0.05

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Estimation of copper(II) and silver(I) by ferrocyanide

The estimation of copper(II) and silver (I) was carried out with a standard solution of potassium ferrocyanide at a pH between 5.0 to 6.5. The maximum amount of copper that could be tolerated was only 10 mg whereas silver was determined even when present in a concentration of 20 mg. Results are given in Table III (Fig. 3).

ACKNOWLEDGEMENTS

Our grateful thanks are due to the University Grants Commission, Government of India, for providing us with the funds for the construction of the high frequency titration apparatus.

SUMMARY

Solutions of potassium chromate, ammonium oxalate and ferrocyanide are used as titrants for the high frequency titration of metal ions. Lead and barium, up to 20 mg, and thallium, up to 50 mg, are estimated with chromate and yield good results. Similarly, ammonium oxalate behaves satisfactorily when the concentration of calcium is not more than 10 mg and that of cerium is between 10 and 40 mg. Copper and silver can be titrated by ferrocyanide only up to a concentration of 10 and 20 mg, respectively. In all cases, the pH of the solution should preferably be between 6.0 and 6.5, though it can be extended in some cases to as low as 5.0.

RÉSUMÉ

Le chromate de potassium, l'oxalate d'ammonium et le ferrocyanure de potassium peuvent être utilisés comme réactifs pour les titrages à haute fréquence du plomb, du baryum et du thallium (avec chromate); du calcium et du cérium (avec oxalate); du cuivre et de l'argent (avec ferrocyanure).

ZUSAMMENFASSUNG

Es werden Methoden zur Hochfrequenztitration von Metall-Ionen beschrieben. Für die Bestimmung von Blei, Barium und Thallium wird eine Kaliumchromatlösung, für Calcium und Cerium eine Ammoniumoxalatlösung und für Kupfer und Silber eine Kaliumferrocyanidlösung verwendet.

REFERENCES

[1] A. K. Majumdar and A. K. Mukherjee, *Anal. Chim. Acta*, 20 (1959) 511.
[2] W. J. Blaedel and H. V. Malmstadt, *Anal. Chem.*, 22 (1950) 734.
[3] W. J. Blaedel and H. V. Malmstadt, *Anal. Chem.*, 23 (1951) 471.
[4] O. I. Milner, *Anal. Chem.*, 24 (1952) 1247.
[5] I. M. Kolthoff and Y. Pan, *J. Am. Chem. Soc.*, 61 (1937) 3402.

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TARTRAZINE, A NEW SELECTIVE REAGENT FOR ZIRCONIUM

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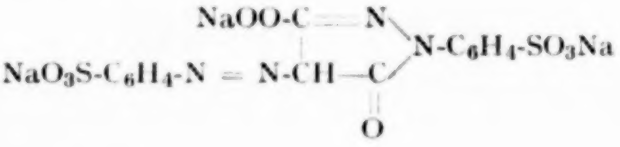
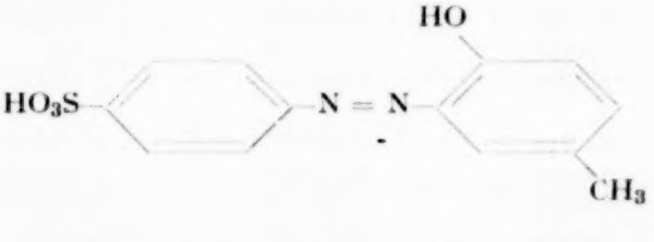
A critical survey of gravimetric methods for zirconium by means of organic reagents shows that few methods permit direct weighing of the precipitate; among them the 8-hydroxyquinoline[1] and mandelic acid[2] methods are the most promising. Owing to the inhomogeneous composition of the precipitates the final weighing form is generally zirconium oxide. In the present paper a new reagent for precipitation of zirconium(IV) is proposed, namely tartrazine:



This reagent was chosen on the basis of the observations made by **Kuznetsov**[3] who examined monoazo dyes and found that the compounds formed in some cases are difficultly soluble precipitates of zirconium and hafnium. The presence of substituting groups in the molecule of the monoazo dyes has a great influence on the properties of the final products. Of particular value is the effect of a hydroxyl group in the *ortho* position adjacent to the azo group.

Another compound which is a very good reagent for zirconium is 2-hydroxy-5-methylazobenzene-4′-sulfonic acid.



Tartrazine contains a carboxylic group situated near to the azo group. This substance reacts in slightly acidic solutions with the salts of zirconium(IV), forming a yellow-orange precipitate. The insolubility of this precipitate in water encouraged us to examine its possibilities for the determination of zirconium.

EXPERIMENTAL

To a zirconium salt solution (nitrate or oxychloride), the concentration of which had been determined by precipitation with ammonium hydroxide and calcination as oxide, an aqueous 2% solution of tartrazine* was added dropwise until precipitation was complete. The pH of the precipitation was 1; but precipitation was also complete in stronger acid medium. The mixture was then heated to 60–80° and filtered through a blue band filter paper. The precipitate was washed with distilled water till the colour of the filtrate became very slight yellow and then calcined to the oxide.

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* The reagent solution used was previously filtered. The reagent is a product of a "Colorom Codlea" factory.

The results obtained are recorded in Table I.

TABLE I

Volume of $ZrOCl_2$ solution ml	*Zr calculated g*	*Zr found g*	*Zr difference mg*
5	0.0050	0.0050	± 0
10	0.0100	0.0099	— 0.1
10	0.0100	0.0100	± 0
10	0.0100	0.0100	± 0
12.5	0.0125	0.0126	+ 0.1
12.5	0.0125	0.0125	± 0
15	0.0150	0.0150	± 0
20	0.0200	0.0200	± 0
25	0.0250	0.0249	— 0.1
30	0.0300	0.0298	— 0.2

Filtration on an A_2-filter crucible was next attempted; the precipitate was dried at 110° for 1 h, and then weighed.

The results obtained are shown in Table II.

TABLE II

Volume of $ZrO(NO_3)_2$ solution ml	*Complex g*	*Zr calculated g*	*Zr found g*	*Zr difference mg*
5	0.0171	0.0055^8	0.0055^8	± 0
5	0.0169	0.0055^8	0.0055^2	— 0.06
10	0.0342	0.0111^6	0.0111^7	+ 0.01
10	0.0340	0.0111^6	0.0111	— 0.06
15	0.0513	0.0167^4	0.0167^5	+ 0.01
15	0.0510	0.0167^4	0.0166^5	— 0.09
20	0.0684	0.0223^2	0.0223^3	+ 0.01
20	0.0680	0.0223^2	0.0222	— 0.12

The factor, 0.32653, corresponds to the formula Zr_3 (tartrazine) $(OOH)_3$.

The results obtained show that the method of precipitation of zirconium with tartrazine is one of the few methods which allows direct weighing of the precipitate.

The specificity of the reagent

Qualitative tests were made of interferences of a series of ions and the following results were obtained.

a. Ions which do not react with tartrazine: aluminium, titanium, uranyl, lanthanum, cerium, potassium, cadmium, zinc, cobalt, nickel, copper, magnesium, sodium,

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lithium, iron, calcium; tests were made especially with those elements which accompany zirconium in alloys and ores.

b. Ions which react with tartrazine giving precipitates or opalescences, which disappear after adding hydrochloric or nitric acid; barium solutions when heated become opalescent, thorium in neutral solution forms a yellow precipitate which dissolves in acid, and mercuric ions form an orange precipitate soluble in nitric acid.

c. The reaction is masked by sulfate and by tartaric or citric acid.

We propose to apply the method to the analysis of alloys and ores.

SUMMARY

A new method for determining zirconium is described, in which tartrazine serves as reagent. The precipitate can be ignited to ZrO_2 or weighed as the complex. The reagent appears to be very selective, and can be used for the determination of zirconium in alloys and ores.

RÉSUMÉ

Une nouvelle méthode est proposée pour le dosage gravimétrique du zirconium au moyen de tartrazine. Grâce à sa bonne spécificité, ce procédé peut être appliqué à des analyses d'alliages et de minerais.

ZUSAMMENFASSUNG

Es wird eine neue Methode beschrieben zur gravimetrischen Bestimmung von Zirkon mit Tartrazin. Da die Reaktion sehr specifisch ist, eignet sie sich zur Bestimmung von Zirkon in Legierungen und Mineralien.

REFERENCES

[1] GR. BALANESCU, *Z. anal. Chem.*, 101 (1935) 101.
[2] R. B. HAHN AND E. S. BAGINSKI, *Anal. Chim. Acta*, 14 (1956) 45.
[3] V. I. KUZNETSOV, *Zhur. Priklad. Khim.*, 13 (1940) 1257.

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SPECTROPHOTOMETRIC DETERMINATION OF GOLD WITH PHENYL-α-PYRIDYL KETOXIME

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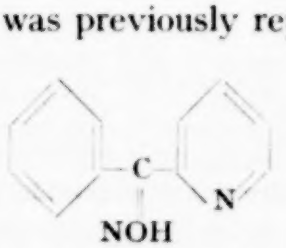
Phenyl-α-pyridyl ketoxime (I) was previously reported as a chelating agent[1] and



(I)

was used for the spectrophotometric determination of palladium[2]. This reagent formed a water insoluble, orange-yellow precipitate with gold(III) which was soluble in chloroform. The present paper describes a procedure for the spectrophotometric determination of gold using phenyl-α-pyridyl ketoxime as the reagent.

The spectrophotometric methods for the determination of gold are relatively few. The spectrophotometric method for the estimation of gold based on the formation of colloidal gold is subject to numerous variables[3]. Both the bromoaurate[4] and the rhodanine[5] methods suffer from interference by the metals with which gold is very frequently associated. Leuco malachite green and o-tolidine are oxidized by gold(III) to produce colored oxidation products. These colored substances have been used for the spectrophotometric determination of gold[6,7]. Recently, MacNulty and Woollard[8] used the rhodamine B method for the estimation of very small amounts of gold.

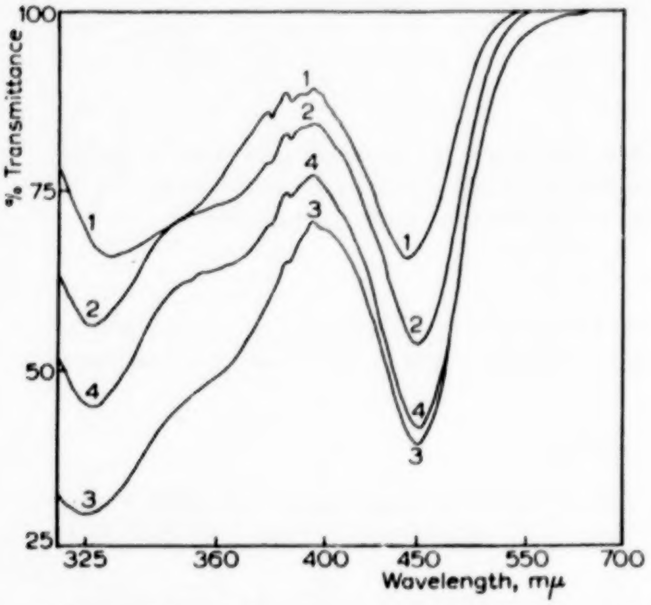


Fig. 1. Spectral curves of gold(III) phenyl-α-pyridyl ketoximate. Gold concentration: 8 p.p.m.; Cell thickness: 1 cm. (1) pH 1.7, (2) pH 2.5, (3) pH 3.2, (4) pH 4.1.

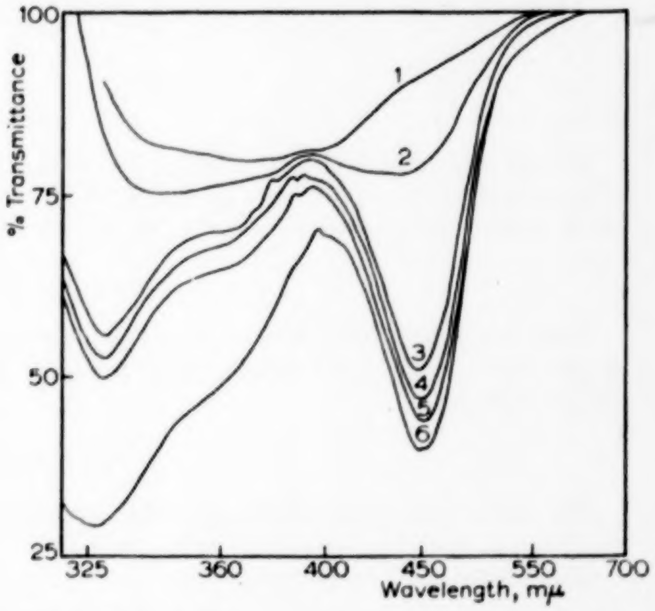


Fig. 2. Spectral curves of gold(III) phenyl-α-pyridyl ketoximate. (1) pH 11.5, (2) pH 10, (3) pH 9.1, (4) pH 7.0, (5) pH 6.0, 5.3, (6) pH 3.2.

Gold(III) reacted with phenyl-α-pyridyl ketoxime to produce a water insoluble chelate. The product was crystalline, orange-yellow in color, and dissolved in chloroform to give a yellow solution. The chloroform extract showed a very sharp light absorption peak at 450 mμ. There was also another absorption band in the ultraviolet region (Figs. 1 and 2). Spectrophotometric determinations were made at 450 mμ because in this region the absorption peak was very sharp and there was also no absorption by the reagent.

EXPERIMENTAL

Spectral studies and light absorbance measurements were made with a Beckman Model DK-1 recording spectrophotometer and a Beckman Model DU spectrophotometer. Matched silica cells of 1-cm light path were used. pH measurements were made with a Beckman Model G pH meter.

Reagent solution. A 1-% solution of phenyl-α-pyridyl ketoxime in 95% ethanol was used as the reagent.

Standard solutions. All chemicals used were of reagent grade.

Gold. The gold solution was prepared from gold(III) chloride; it was $1M$ with respect to hydrochloric acid. The solution was standardized by precipitating the gold with hydroquinone and weighing as metal according to Beamish[9].

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The solutions of other cations were prepared from their sulfates, chlorides, and nitrates. Their strengths were determined by standard procedures. The osmium solution was prepared by starting with osmic acid. The solutions of the anions were prepared from their potassium and sodium salts. The various buffer solutions were prepared according to VOGEL[10].

TABLE I

WAVELENGTHS OF LIGHT ABSORPTION PEAKES OF A NUMBER OF METAL PHENYL-α-PYRIDYL KETOXIMATES IN CHLOROFORM

Cation	*Wave-length of absorption peakes mμ*	*Remark*
Fe^{+2}	530	Absorption rapidly increases after 460 mμ
Co^{+2}		Absorption rapidly increases after 600 mμ
Ni^{+2}		Absorption rapidly increases after 550 mμ
Cu^{+2}	475 350	
Pd^{+2}	410 327	
Au^{+3}	450 325	

Light absorption spectrum of gold phenyl-α-pyridyl ketoximate and effect of pH on chelation and extraction

The spectral characteristics of the phenyl-α-pyridyl ketoximates of different cations were reported in an earlier communication[2]. Table I summarizes the regions of maximum absorption of the different chelates. The solutions for the present studies were prepared as follows: 200 μg (8 p.p.m. in the final solution) of gold were taken in a 50-ml beaker. 1 ml of the 1% reagent solution was then added to the gold solution followed by 2 ml of water. The pH of the solution was then adjusted with sodium carbonate or sodium bicarbonate solution and the pH was recorded with a pH meter. The solution was then transferred to a 50-ml separatory funnel using a minimum volume of water for washing the beaker. The volume of the solution was maintained approximately at 10 ml. The solution was then extracted three times with chloroform using 5 ml chloroform each time. The volume of the chloroform extract was made up to 25 ml with chloroform and the light transmittance of the chloroform extract was measured with a Beckman DK-1 spectrophotometer. The results are shown in Figs. 1 and 2. Any gold left in the aqueous phase was detected by applying the dimethylaminobenzylidenerhodanine spot test[11]. Prior to applying the spot test, the aqueous phase was evaporated almost to dryness and the organic reagent was decomposed by treating the residue with 5 ml aqua regia and evaporating to dryness. The treatment with aqua regia was repeated three times. The final residue was extracted with 5 ml of water. The spot test was carried out with this solution. No positive test for gold was given by the aqueous phase when the extractions were performed between pH 2.5 and 9.1. The spectral curves (Fig. 1 and 2) also indicated that the optimum pH for chelation and extraction was between 3 and 6. At pH 11.5 there was no chelation as was evidenced by the absence of the characteristic peakes.

Effect of the buffers

200 μg of gold (8 p.p.m. in the final solution) were taken in a 50-ml beaker. 1 ml of the reagent solution was then added to it followed by 3 ml of water. The pH of the solution was then adjusted between 3 and 9 by the addition of sodium carbonate or bicarbonate solution. 1 ml of the appropriate buffer solution was then added. Acetate, phosphate, borate, ammonia-ammonium chloride and tartrate buffers were used. The solution was then transferred to a 50-ml separatory funnel using a minimum volume of water to wash the beaker. The solution was then extracted three times with chloroform using 5 ml of chloroform each time. The volume of the chloroform extract was then made up to 25 ml with chloroform and the absorption spectrum of the chloroform extract was studied using a Beckman Model DK-1 spectrophotometer. Excepting the case when extraction was performed from the tartrate buffered system, in all cases the spectral characteristics of the chloroform extracts were exactly identical whether the extraction was performed from the buffered or the corresponding unbuffered solution of same hydrogen ion concentration. When the tartrate buffer was used there was a considerable decrease in absorbance all along the spectrum. This probably was due to the partial reduction of gold.

TABLE II

EFFECT OF REAGENT ON THE ABSORBANCE OF THE CHLOROFORM EXTRACT OF THE GOLD CHELATE

Amount of gold mg	*Amount of reagent mg*	*Amount of reagent / Amount of gold*	*Absorbance*
0.2	0.5	2.5	0.08
	1.0	5.0	0.14
	5.0	25.0	0.40
	10.0	50.0	0.40
	20.0	100.0	0.40
	50.0	250.0	0.38
	100.0	500.0	0.28

Effect of reagent, temperature, and time

The amount of gold used, the dilution, and the general procedure for extraction were the same as in previous studies. The pH of all the solutions was adjusted between 3.5 and 4.5 before the extraction and no buffer was used. During the study of the effect of the reagent, the amount of reagent added was varied (see Table II). During the study of the effect of temperature and time, 1 ml of the 1% reagent solution was used. The temperature of the chloroform extract between 0 and 45° was without any effect. There was no change in absorbance of the chloroform extract in two weeks. The color development was instantaneous. All absorbance measurements were made at 450 mμ and against proper blank solutions.

Beer's law

The gold solution and 2 ml of the reagent solution were taken in a 50-ml beaker, the solution was diluted to about 5 ml and the pH of the mixture adjusted between 3.5 and 4.5 by the addition of sodium bicarbonate solution. The solution was then transferred to a 50-ml separatory funnel using a minimum volume of water to wash the beaker. The solution was then extracted 3 times with chloroform using 5 ml of chloroform each time and the final volume of the chloroform extract was made up to 25 ml with chloroform and the absorbance measured at 450 mμ. All measurements were made against a blank prepared similarly except that it did not contain any gold. The results are shown in Table III.

TABLE III

STUDY OF BEER'S LAW

Amount of gold μg	*Concn. of gold p.p.m.*	*Absorbance*	*Specific absorptivity*[a]	*Mean specific absorptivity*
50	2	0.08	40.0	47.9
100	4	0.20	50.0	
150	6	0.28	46.6	
200	8	0.40	50.5	
250	10	0.50	50.0	
300	12	0.58	48.3	
350	14	0.70		
400	16	0.80	50.0	

[a] Specific absorptivity $= \frac{\text{Absorbance}}{\text{mg of gold/ml} \times \text{cell thickness}}$

Effect of diverse ions

Binary mixtures were prepared containing 200 μg of gold and 10 mg of a second cation. The mixture treated with 2 ml of the reagent solution. The subsequent steps in the procedure were the same as in the case of studying Beer's law. The absorbance of the chloroform layer was measured at 450 mμ. Alkaline earth metal ions, Ag^+, NH_4^+, Cd^{+2}, Pb^{+2}, Mn^{+2}, VO^{+2}, Al^{+3}, Bi^{+3}, Fe^{+3}, Ru^{+4}, Rh^{+3}, Os^{+4}, Ir^{+4} and Pt^{+4} did not interfere. The precipitate thrown down during the study, Ag^+, Bi^{+3}, and Fe^{+3}, separated at the interface of the two phases and was removed by dry filtration. Interference due to Cu^{+2}, Co^{+2}, and Ni^{+2} was eliminated by using 0.1*M* EDTA solution. During these studies the reference gold sample as well as the blank were treated with identical amounts of EDTA solution. The presence of EDTA decreased the absorbance of the gold chelate by about 5%. Pd (II), Hg^{+2}, Fe^{+2}, Cn^-, Br^-, I^- and the organic anions like oxalate, citrate and tartrate seriously interferred with the method.

Sensitivity

Limit of identification = 1 μg
Limit of dilution = 1:1,000,000

DISCUSSION

Phenyl-α-pyridyl ketoxime was found to be a sensitive reagent for the spectrophotometric determination of gold. There was no interference by the ions with which gold is usually associated. Beer's law was obeyed between 2 and 16 p.p.m. of gold. Under the present experimental conditions the optimum concentration range for a minimum photometric error was between 4 and 10 p.p.m. In the last column of Table III the specific absorptivity defined as

$$\frac{\text{Absorbance}}{\text{mg of gold/ml} \times \text{cell thickness}}$$

is given instead of the molar extinction coefficient. The present investigator is not yet certain whether gold and reagent combine in the ratio of 1 mole to 2 moles or 1 mole to 3 moles. In any case, the molar extinction coefficient will be of the order 10^4. The values of the specific absorptivity show a high reproducibility of the method. The results in Table II show that an amount of reagent between 5 and 250 times the amount of gold produces a maximum color intensity in the chloroform extract.

The results of the investigation about the structure of gold and other metal phenyl-*α*-pyridyl ketoximates and the other analytical applications of this reagent will be published in subsequent communications.

ACKNOWLEDGEMENT

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SUMMARY

A method is described for the spectrophotometric determination of gold in the concentration range of 2 to 16 p.p.m. using phenyl-*α*-pyridyl ketoxime as the reagent. The reagent permits to detect 1 μg of gold in 1 ml of a solution. The method is particularly free from interference by the ions with which gold is frequently associated.

RÉSUMÉ

Une méthode spectrophotométrique sensible et sélective est décrite pour le dosage de l'or. On utilise comme réactif l'oxime de la phényl-*α*-pyridylcétone.

ZUSAMMENFASSUNG

Es wird eine empfindliche und selektive spektrophotometrische Methode zur Bestimmung von Gold mit Hilfe von Phenyl-pyridyl-ketoxim beschrieben.

REFERENCES

[1] B. SEN, *Chem. & Ind.* (*London*), (1958) 562.
[2] B. SEN, *Anal. Chem.*, 30 (1959) 881.
[3] C. G. FINK AND G. L. PUTNAM, *Ind. Eng. Chem., Anal. Ed.*, 14 (1942) 468.
[4] W. A. MCBRYDE AND J. H. YOE, *Anal. Chem.*, 20 (1948) 1094.
[5] E. B. SANDELL, *Anal. Chem.*, 20 (1948) 253.
[6] W. B. POLLARD, *Analyst*, 44 (1919) 94.
[7] L. M. KUL'LUNG, *Zavodskaya Lab.*, 5 (1936) 170.
[8] B. J. MACNULTY AND L. D. WOOLLARD, *Anal. Chim. Acta*, 13 (1955) 154.
[9] F. E. BEAMISH, J. J. RUSSELL AND J. SEATH, *Ind. Eng. Chem., Anal. Ed.*, 9 (1937) 174.
[10] A. I. VOGEL, *A Text Book of Quantitative Inorganic Analysis*, Longmans, Green and Co., London, 1940.
[11] F. FEIGL, *Spot Tests*, Vol. I, Elsevier Publishing Company, Amsterdam, 1954, p. 122.

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DETERMINATION OF COPPER AND ZINC IN METALLURGICAL PRODUCTS BY AUTOMATIC DERIVATIVE SPECTROPHOTOMETRIC TITRATIONS

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The methods often used for the determination of copper and zinc in metallurgical products are quite time-consuming and many attempts have been made to shorten them. Complexometric titrations using ethylenediaminetetraacetic acid (EDTA) as titrant and metal indicators for visual end-point detection have been tested and have provided good results[1-6].

Recently the authors described an automatic titration method for the determination of Ca and Mg[7]. The subjective evaluation of end-points was eliminated by using the automatic derivative spectrophotometric end-point detection system provided in the new, commercially available "Spectro-Electro" titrator[8] (E. H. Sargent Co., Chicago, Ill.). The same titrator and spectrophotometric end-point detection system has been found to be well suited for the automatic titration of Cu and Zn in brasses and bronzes.

The Cu^{+2} in an aliquot of dissolved sample reacts with excess iodide at pH 4.0 and the liberated iodine is automatically titrated. The UV absorption band of iodine between 350 and 400 mμ provides an excellent end-point signal for termination of the titration[9]. Another aliquot of sample is also buffered at pH 4.0 and both Cu and Zn are automatically titrated with EDTA as titrant and 1-(2-pyridylazo)-2-naphthol (PAN) as indicator; the Zn is calculated by difference.

The automatic end-points are reproducible and accurate within 0.01 ml of 0.025*M* thiosulfate solution and 0.02 ml of 0.01*M* EDTA solution, and the results check closely with standard values. The total time required for a complete analysis of both Cu and Zn is about 20 min, including weighing, addition of reagents, separations, titrations and calculations. Interfering ions are removed by precipitation as the hydroxides in the presence of an excess of ammonium hydroxide.

APPARATUS

The Sargent-Malmstadt "Spectro-Electro" titrator was used[8]. The photoconductive detector circuit supplied with the titrator was connected according to instructions in the instrument manual.

Since two different titrants are required for the titrations, it is desirable to fix two delivery tips in correct position relative to the stirrer, and to connect the top end of each delivery tip to its respective buret tip with a short piece of gum rubber or neoprene tubing. Each tubing passes through a separate buret valve. A buret valve and suitable buret for each titrant are mounted on each of the two support rods.

A second buret valve and switching arrangement for selecting either titrant are not part of the standard equipment. However, another buret valve can be obtained and the switching device easily assembled. A diagram of the titrant switching system is shown in Fig. 1. The parts are mounted in a small $3^1/_2'' \times 2'' \times 2''$ aluminum box with the pilot lights and switch protruding through one side and the sockets available from the opposite side. The switch box is mounted between the two rods holding the two burets, and the valves for controlling delivery of the titrants are plugged into their proper outlets. A 3′ cord connects the switch box to the valve outlet in the back of the Spectro-Electro titrator. The delivery of the proper titrant is determined by the position of the toggle switch marked "$Na_2S_2O_3$" in one position and "EDTA" in the other position.

A 5-ml buret, graduated in 0.01-ml divisions and equipped with delivery and refill teflon stopcocks and titrant reservoir was used for the $Na_2S_2O_3$ titrant and a 10-ml self-zeroing buret also equipped with delivery and refill teflon stopcocks and titrant reservoir was used for the EDTA titrant. Both burets are products of Fischer-Porter Co. (Hatboro, Pennsylvania).

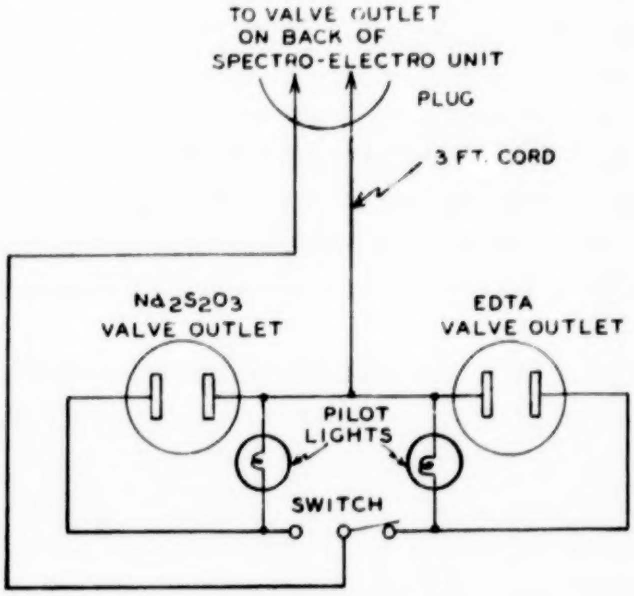

Fig. 1. Titrant selector.

REAGENTS

Standard $10^{-2}M$ copper solution. Dissolve 0.6354 g reagent grade copper sheet in slight excess of concentrated HNO_3 and dilute to the mark in 1-l volumetric flask with deionized water. 1 ml contains 0.6354 mg copper.

Zinc solution. Dissolve 0.6538 g of reagent grade zinc (Grannular, 20 mesh) in 1:1 HCl and dilute up to 1 l with deionized water. 1 ml contains 0.6538 mg zinc.

EDTA solution. The $0.01M$ EDTA solution is prepared by dissolving approximately 3.723 g of disodium salt of ethylenediaminetetraacetic acid (EDTA) in deionized water and diluting up to 1 l. This solution is standardized against the standard copper solution and stored in polyethylene bottles.

Thiosulfate solution. The $0.025M$ thiosulfate solution is prepared by diluting a commercially available solution of thiosulfate (Acculute).

Buffer solution. Mix 162 ml of $1N$ acetic acid with 38 ml of $1N$ sodium acetate.

PAN indicator. 0.1% solution in methanol.

PROCEDURE

Preparation of automatic titrator. The "Spectro-Electro" titrator is switched to the "Spectro" position; the polarity switch thrown to position 1; the filter wheel turned to the 575 mμ position; the pegs in the base set to properly position the 50-ml beakers; the small stirrer, delivery tips, and burets connected; and the delivery set at about 3 ml/min for both titrants. The same conditions are suitable for both end-points, but in the case of the iodine titration a visible cut-off filter (Cobalt glass #5970, Corning Glass Co., Corning, N. Y.) is placed in the auxiliary filter holder in the titration compartment to allow only the transmission of the UV band at about 390 mμ.

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Standardization of EDTA solution. Pipet a 5-ml aliquot of standard copper solution into a 50-ml beaker, dilute to about 25 ml with a 1:1 mixture of ethanol and water, adjust pH to about 4.0 with conc. ammonia (use pHydrion paper), add 2 ml of buffer solution and heat the solution to boiling. Add 3 drops of the PAN indicator and insert beaker in automatic "Spectro" titrator. Check that the visible cut-off filter is *not* in the light path and the titrant selector switch is in "EDTA" position; push the automatic start button to start stirring and delivery of titrant, and read the buret after automatic termination at the end-point.

Standardization of thiosulfate solution. Pipet a 10-ml aliquot of standard copper solution into a 50-ml beaker, dilute to approximately 25 ml with deionized water from which oxygen has been expelled by CO_2, adjust pH to approximately 4.0 with conc. ammonia, add 2 ml of buffer solution and 4–5 g of potassium iodide. Insert beaker in titrator, check that the visible cut-off filter *is* in the light path, the titrant selector switch is in "$Na_2S_2O_3$" position and the buret filled to the zero mark, turn on stirring and when the cuprous iodide is completely dissolved (about one min) and the solution clear, push the start button to start the delivery of thiosulfate solution and read the buret after automatic termination at the end-point.

Preparation of brass and bronze samples. Dissolve an accurately weighed sample of about 0.50 g of brass or bronze with 8 ml of 1:1 nitric acid in a 150-ml beaker. Heat gently and evaporate to about 3–4 ml. Dilute to approximately 80 ml with deionized water, heat nearly to boiling and adjust to pH 8–9 with conc. ammonia to precipitate sesquioxides of lead, manganese, and tin. Transfer the contents to 40-ml centrifuge tubes and centrifuge at about 2000 r.p.m. for 2–3 min. Transfer the supernatent liquid to a 500-ml volumetric flask, dissolve the precipitate with 1:1 HCl, reprecipitate with ammonia and centrifuge for one min. Transfer the supernatent liquid into the 500-ml flask and dilute up to volume with deionized water. This solution is used for both titrations.

Titration of copper. The same procedure as given for the standardization of thiosulfate solution is followed, except that the adjustment to about pH 4.0, prior to the addition of the buffer, is done with 1:3 HCl, because the solution is already ammoniacal.

Titration of total copper and zinc. Nearly the same procedure as given for the standardization of EDTA solution is followed even though zinc is also present. The only difference is that the adjustment to about pH 4.0, prior to the addition of the buffer, is done with 1:3 HCl, because the solution is already ammoniacal.

Zinc. Zinc is calculated by subtracting the volume of EDTA equivalent to the amount of copper found in the copper titration from the volume of EDTA used in the total Cu and Zn titration. A blank of 0.05 is also subtracted from the remaining volume.

CALCULATIONS

The percentages of copper and zinc can be rapidly calculated by equations (1) and (2), respectively, if the weighed sample is dissolved and made up to volume in a 500-ml volumetric flask, and a 10-ml aliquot taken for the titration of copper and a 5-ml aliquot taken for the titration of total copper and zinc.

$$\frac{A \times (B - 0.02) \times 5}{C} = D = \%\ \text{Cu} \quad \text{(1)}$$

$$\frac{G \times (E - F - 0.05) \times 10}{C} = \%\ \text{Zn} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

where,

A = mg of copper per ml of thiosulfate solution ($A = \frac{6.354}{H - 0.02}$, where H = ml of thiosulfate solution used in the standardization of thiosulfate solution).

B = ml of thiosulfate titrant used for the titration of copper in the sample.

C = weight of sample in grams.

E = ml of EDTA solution used in the titration of total copper and zinc.

F = ml of EDTA solution equivalent to the amount of copper found ($F = \frac{K - 0.05}{H - 0.02}(B - 0.02)$; where K = ml of EDTA solution used in the standardization of EDTA solution).

G = mg of zinc per ml of EDTA solution ($G = \frac{3.269}{K - 0.05}$).

RESULTS AND DISCUSSION

Analysis of solutions containing known concentrations of copper and zinc in different amounts and in different ratios gave the results shown in Table I. It is seen that the average absolute error is less than 0.003 mg for Cu, which is equivalent to about 0.002 ml of 0.025*M* thiosulfate solution, which is about the reading error of the 5-ml buret for the copper titration. The average absolute error is less than 0.007 mg for Zn, which is equivalent to about 0.01 ml of 0.01*M* EDTA solution, and this is approximately the reading error of the 10-ml buret used for the total copper and zinc titration.

TABLE I

AUTOMATIC TITRATION RESULTS FOR SAMPLES CONTAINING KNOWN AMOUNTS OF COPPER AND ZINC

Sample No.	*Copper*			*Zinc*		
	Taken, mg	*Found, mg*	*Difference*	*Taken, mg*	*Found, mg*	*Difference*
1	3.177	3.178	+0.001			
2	3.177	3.176	—0.001			
3	3.177	3.179	+0.002	1.961	1.956	—0.005
4	3.177	3.175	—0.002	1.961	1.960	—0.001
5	1.906	1.914	+0.008	1.961	1.953	—0.008
6	1.906	1.911	+0.005	1.961	1.947	—0.014
7	6.354	6.359	+0.005	0.654	0.664	+0.010
8	6.354	6.355	+0.001	0.654	0.660	+0.006
9	0.635	0.635	0.000	3.269	3.264	—0.005
10	0.635	0.633	—0.002	3.269	3.267	—0.002

Satisfactory results were obtained in the analysis of National Bureau of Standards brass and bronze samples (Table II). The average deviation is about 0.1% for both

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TABLE II

AUTOMATIC TITRATION RESULTS FOR COPPER AND ZINC IN NBS BRASS AND BRONZE SAMPLES

NBS Number	*Cu %*			*Zn %*		
	Found	*Reported*	*Difference*	*Found*	*Reported*	*Difference*
Bronze 628	57.6			37.9		
	57.5			38.0		
	57.4			38.1		
	av. 57.5	57.39	+0.11	av. 38.0	37.97	+0.03
Silicon bronze 158	90.9			1.8		
	90.9			2.0		
	91.1			2.2		
	av. 91.0	90.86	+0.14	av. 2.0	2.07	−0.07
Bronze 164	63.5			21.1		
	63.3			21.4		
	63.2			21.3		
	av. 63.3	63.76	−0.46	av. 21.3	21.89	−0.59
Sheet bronze 37[a]	70.4	70.29	+0.11	27.1	26.89	+0.21
Cast bronze 52b[a]	88.5	88.25	+0.25	3.0	2.96	+0.04

[a] Average of triplicate results with the same precision as shown by the three other samples.

copper and zinc. The large negative errors for both Cu and Zn in NBS bronze sample #164 are due to its large content of interfering ions (6.21% Al, 2.52% Fe, 4.68% Mn) which results in a large coprecipitation of both copper and zinc during precipitation of the interfering ions. A double or even a third reprecipitation is recommended in samples very rich in interfering elements.

The delivery rate of the titrant was adjusted in the range of about 3 ml/min for the standardization of the EDTA solution and of the thiosulfate solution and all the titrations of copper and zinc samples. The adjustment of rate can be done with either a suitable capillary delivery tip or varying the opening of the teflon stopcock and pinch-off valve. At this delivery rate the titration time for total Cu and Zn is about 2 to 3 min for the analyzed samples, and the temperature of the solution at the end of the titration is about 55–65°. Under these conditions a blank of 0.05 ml of 0.01*M* EDTA solution is applied because of the small but reproducible overshooting of the equivalence point, and a blank of 0.02 ml is applied when thiosulfate is used as titrant.

The use of an excess of potassium iodide to dissolve the cuprous iodide, and stirring the solution before the start of the titration until it is clear are recommended in order to assure a large end-point signal sufficient to automatically terminate the titration. However, a turbid solution, due to incomplete solution of cuprous iodide can be used, but in this case an amplification of the small signal might be required to assure automatic termination at the end-point.

To minimize air oxidation of iodide during the titration of iodine, the solution is buffered at pH 4.0 and oxygen-free water is used for the dilution of the sample. The use of iodine as its own indicator simplifies the procedure[9]. At a pH of 4.0 sharp end-points were also assured in the titration of total Cu and Zn.

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An attempt was made to titrate Cu and Zn successively in the same aliquot sample. The solution was boiled after the titration of iodine with thiosulfate, and PAN indicator was added for the titration of zinc with EDTA. However, this reaction is quite sluggish and often the end-points were missed.

The thiosulfate solution can also be standardized against standard iodine solution (Acculute) or accurately weighed iodine. The EDTA solution was also standardized against standard $CaCO_3$ with Calcon as indicator, as previously reported[8]. The standardization methods against copper and $CaCO_3$ agreed within 0.2%.

Since the 0.5-gram samples were diluted to 500 ml and 5 and 10-ml aliquots taken for the EDTA and thiosulfate titrations, respectively, only 5 and 10 mg of actual sample were present for the two titrations.

ACKNOWLEDGEMENT

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SUMMARY

Direct automatic derivative spectrophotometric titration procedures for copper and zinc in brasses and bronzes are described. Copper reacts with excess iodide and the liberated iodine is automatically titrated with thiosulfate using the UV absorption band of iodine for end-point detection. Total copper and zinc is automatically titrated with EDTA using PAN as indicator, and zinc is found by difference. The automatic termination of the titrations eliminates the subjective evaluation of the end-points, and the entire procedure is simple, precise and accurate. The total time required for determining copper and zinc in brass or bronze is about twenty minutes.

RÉSUMÉ

Une méthode spectrophotométrique automatique rapide est proposée pour le dosage du cuivre et du zinc dans des laitons et des bronzes. Le cuivre est traité par un excès d'iodure; l'iode formé est titré automatiquement par spectrophotométrie au moyen de thiosulfate. La somme des teneurs en cuivre et zinc est ensuite déterminée automatiquement par titrage au moyen d'acide éthylènediaminotétracétique. La teneur en zinc est obtenue par différence.

ZUSAMMENFASSUNG

Es wird eine rasche automatische spektrophotometrische Methode zur Bestimmung von Kupfer und Zink in Messing und Bronzen beschrieben. Das Kupfer reagiert mit zugesetztem Jodid unter Bildung von freiem Jod, das mit Thiosulfat automatisch spektrophotometrisch titriert wird. Dann wird Kupfer + Zink durch automatische Titration mit EDTA bestimmt und der Zinkgehalt aus der Differenz errechnet.

REFERENCES

[1] H. Flaschka, *Mikrochemie ver. Mikrochim. Acta*, 39 (1952) 38.
[2] K. L. Cheng and R. H. Bray, *Anal. Chem.*, 27 (1955) 782.
[3] H. Flaschka and H. Abdine, *Mikrochim. Acta*, (1956) 770.
[4] K. L. Cheng, *Anal. Chem.*, 30 (1958) 243.
[5] J. Kinnunen and B. Merikanto, *Chemist Analyst*, 41 (1952) 4.
[6] J. T. McCall, G. K. Davis and T. W. Stearns, *Anal. Chem.*, 30 (1958) 1345.
[7] H. V. Malmstadt and T. P. Hadjiioannou, *Anal. Chim. Acta*, 19 (1958) 563.
[8] E. H. Sargent Co., *Scientific Apparatus and Methods*, 10 (1958) No. 2, 1.
[9] H. V. Malmstadt and D. A. Vassallo, *Anal. Chim. Acta*, 16 (1957) 455.

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SPECTROPHOTOMETRIC DETERMINATION OF IRON WITH 2-HYDROXY-3-NAPTHOIC ACID

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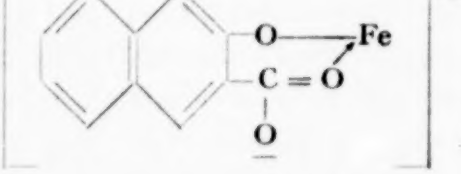
As early as 1834, the phenolic derivatives were tested[1] for their presence by their colour reaction with ferric ion, which subsequently was used for the detection of aromatic hydroxy derivatives. Salicylic acid[2] was the first of the aromatic hydroxy acids to be used for the quantitative determination of iron. Sulphosalicylic acid[3], salicyl aldoxime[4] and β-resorcylic acid[5] were other reagents used for the same purpose.

During our study of the phenolic derivatives[6,7] as colour-forming reagents, 2-hydroxy-3-napthoic acid has been found to behave as a very sensitive and highly selective reagent in its colour reaction with iron. The iron complex is soluble in water, but the excess reagent that is present along with the complex, comes out of solution. This, however, is prevented by the addition of gelatin, which as a peptising colloid stabilises and keeps the reagent as well as the complex in solution. The colour system so formed shows the maximum intensity of the colour at pH 2.9 to 3.1 with the maximum and minimum absorption regions, respectively, at 590 mμ and 420 mμ, within the range of 400 to 650 mμ. The sensitivity of the reaction is 0.25 μg/cm^2 (practical) and 0.025 μg/cm^2 (SANDELL). The system obeys Beer's law up to 24 p.p.m. of iron and the optimum range is from 4 to 20 p.p.m. of iron, where the per cent relative analysis error per 1% absolute photometric error is 2.9. The composition of the complex, as elucidated by the continuous variation, slope ratio and molar ratio methods, indicate that in solution the complex contains the metal and the reagent in the ratio of 1 : 1. The empirical formula of the complex may be suggested as: $[Fe(C_{11}H_7O_3)]^{+2}$ and may be represented structurally as:



The molar extinction coefficient of the complex is 2212 and the instability constant is about $4.29 \cdot 10^{-4}$.

Coloured ions or those ions that give coloured products are tolerated to a limited extent, while the complex-forming agents, like phosphate, fluoride, oxalate, citrate and tartrate, interfere with the determination of iron.

EXPERIMENTAL

Apparatus and solutions

The U.V. Spectrophotometer with 10.0-mm quartz transmission cells and the pH indicator were the same as used in a previous work[7].

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Reagent solution

The reagent 2-hydroxy-3-napthoic acid of British Drug House, Ltd., was crystallised several times from alcohol till its melting point was between 222 and 223°. Because of its lower solubility in water, a 0.1% solution of the reagent in 95% ethyl alcohol was prepared and was used as the reagent solution throughout the work.

Iron solution

A standard solution of ferric nitrate was prepared from an Analar variety of the sample of British Drug House, Ltd. A weighed amount of the sample was dissolved in 100 ml water with the addition of 5 ml of nitric acid and was diluted to 1000 ml. The iron content of the solution, as determined gravimetrically, was found to be 1.727 mg/ml. Weaker solutions were prepared, as needed, by dilution.

Buffer solution

A sodium acetate–hydrochloric acid buffer of pH 3.0 was obtained by mixing normal solutions of sodium acetate (50 ml) and hydrochloric acid (48.5 ml) and diluting the solution with water to 250 ml.

Equimolecular solutions of ferric ion, the reagent for the study of the composition of the complex and a 0.2% (w/v) solution of gelatin were the other solutions prepared.

Other chemicals and solutions of diverse ions used were identical with those reported earlier[7].

Absorbance curves

An aliquot quantity of the iron solution was taken in a 25-ml volumetric flask and to it were added, in succession, 1 ml of the gelatin solution, 3 ml of the reagent solution, and 2 ml of the buffer to adjust its pH to 3.0. After dilution to 25 ml with water and thorough mixing, the absorption of the blue-coloured complex was measured against a reagent blank. Curves A and B in Fig. 1 show the maximum and minimum absorption regions of the colour system corresponding to 7.5 and 10.0 p.p.m. of ferric ions respectively; the regions in both cases are 590 mμ and 420mμ respectively, where the reagent has no absorption.

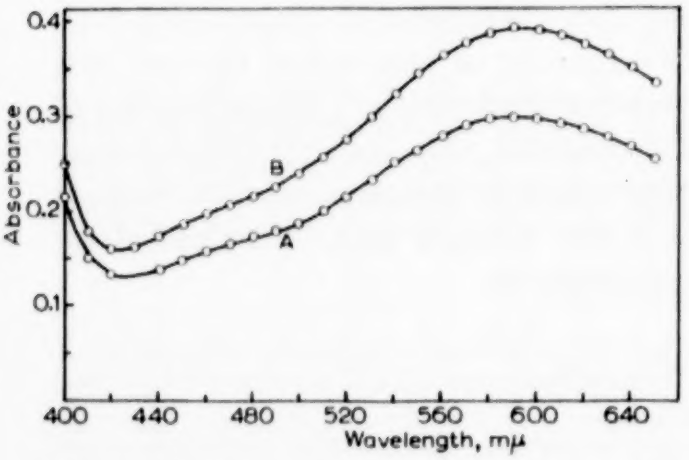


Fig. 1. Absorbance curves, A. 7.5 p.p.m. Fe; B. 10.0 p.p.m. Fe.

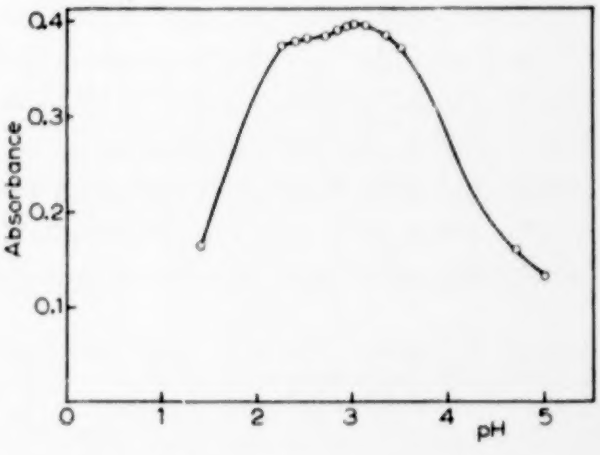


Fig. 2. Effect of pH; 10 p.p.m. Fe.

Effect of pH, reagent and time

The colour intensity is somewhat sensitive to changes in hydrogen concentration. Spectrophotometric measurements of a series of solutions with pH varying from 1.4 to 5.0 and always containing 10 p.p.m. of ferric ion, 1 ml of the gelatin solution and 3 ml of the reagent in a total volume of 25 ml, indicated that the colour intensity was at its maximum when the pH of the system was between 2.9 and 3.1. This restricted pH range necessitated the use of the buffer solution (2 ml) to adjust the pH of the system to 3.0. The optical density variation with pH is shown in Fig. 2.

Similar studies of the effect of the reagent concentration on the colour system formed with 10 p.p.m. of ferric ion, 1 ml of the gelatin solution, 0.25 to 5.0 ml of the reagent solution and 2 ml of the buffer solution in a total volume of 25 ml were made and from the curve in Fig. 3 it appears that the maximum intensity of the colour is reached when the amount of reagent is only 2 ml of 0.1%, in a volume of 25 ml. For all subsequent measurements 3 ml of the reagent were always used.

The colour intensity of the iron–reagent complex changes with time, but for the first one hour the change is negligible as is evident from the curve in Fig. 3 and hence the optical density of the colour system was invariably measured immediately after preparation.

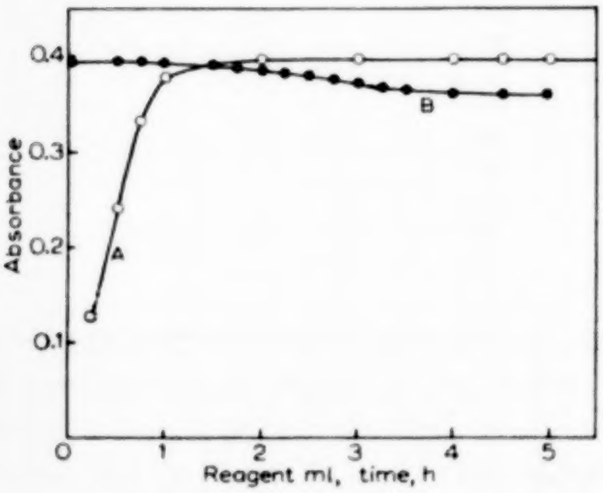


Fig. 3. A. Effect of reagent; B. Effect of time.

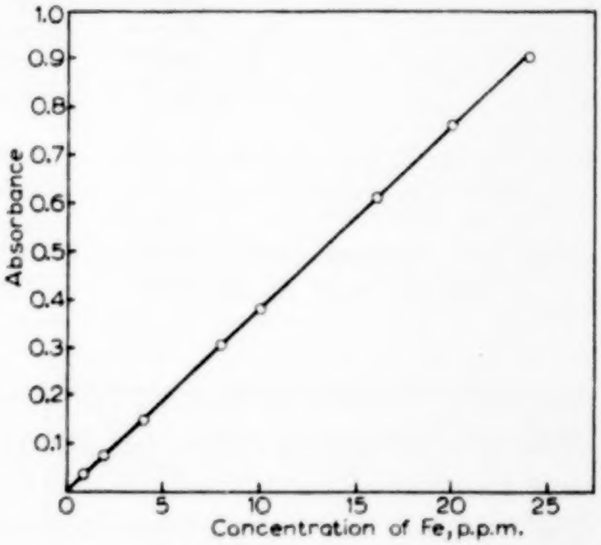


Fig. 4. Beer's law curve.

Beer's law, optimum range and photometric error

For the verification of Beer's law, optical densities at 590 $m\mu$ of a number of colour systems, with different quantities of ferric ion, measured against a water blank, were plotted against the respective concentrations of iron Fig. 4. Thus the systems were found to obey Beer's law with any iron concentration of 1 to 24 p.p.m.

Optimum range and accuracy in the photometric analysis of the proposed method were determined in the same way as described in the previous paper[7]. The optimum concentration range as obtained from the steep of the curve in Fig. 5 is from 4 to 20 p.p.m. of iron and the relative analysis error per 1% absolute photometric error for this range is 2.9%.

Effect of diverse ions

After the addition of the ion whose effect was to be studied, to the iron solution containing 10 p.p.m. of iron, the gelatin solution (1 ml), reagent solution (3 ml), and the buffer solution (2 ml) were added in the order stated. This was then diluted to 25 ml with water and its absorbancy was measured at 590 $m\mu$. An ion was considered to interfere if the resulting solution differed by 0.005 in optical density (*cf.* Table I).

Such ions as phosphate, fluoride, oxalate, phthalate, citrate and tartrate which form complexes with ferric ion interfere. They either reduce the sensitivity or prevent the colour formation completely. Interference due to titanium was avoided by lowering the pH to 2.5.

TABLE I

Ion	*Added as*	*Limiting concentration p.p.m.*
Al^{+3}	$Al(NO_3)_3$	100
Ca^{+2}	$Ca(NO_3)_2$	100
Co^{+2}	$Co(NO_3)_2$	25
Cr^{+3}	$Cr(NO_3)_3$	30
Cu^{+2}	$Cu(NO_3)_2$	40
Cd^{+2}	$Cd(NO_3)_2$	100
Hg^{+2}	$HgCl_2$	30
Mg^{+2}	$MgCl_2$	60
Mn^{+2}	$MnCl_2$	40
Ni^{+2}	$Ni(NO_3)_2$	10
Th^{+4}	$Th(NO_3)_4$	50
Ti^{+4}	$Ti(SO_4)_2$	10
UO_2^{+2}	$UO_2(NO_3)_2$	20
Zn^{+2}	$Zn(NO_3)_2$	50
Zr^{+4}	$ZrOCl_2$	5

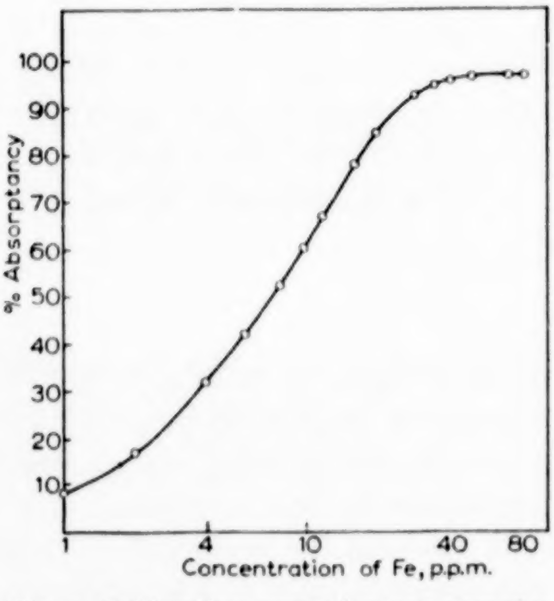


Fig. 5. Calibration curve for iron complex.

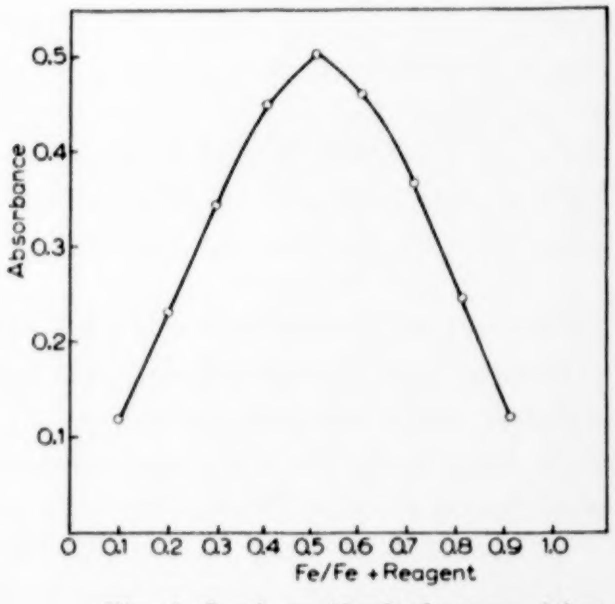


Fig. 6. JOB's method of composition.

Composition of the iron-2-hydroxy-3-napthoic acid

For the evaluation of the composition of the complex, the absorption of the mixtures (keeping the total volume constant) of equimolecular solutions ($1.33 \cdot 10^{-3}M$) of ferric ion and the reagent was measured at 590 mμ at which the iron and the reagent had no absorption. Fig. 6 is the true graphical representation of the absorption as plotted against the increasing amount of the ferric ion. The maximum indicates the formula of the complex to be $[Fe(C_{11}H_7O_3)]^{+2}$ where the iron and the reagent are in a ratio of 1 : 1.

Similar studies by the molar ratio method with equimolecular solutions ($5.32 \cdot 10^{-3}M$) of the ferric ion and the reagent yielded the identical composition of the complex.

References p. 52

Fig. 7, obtained with a fixed quantity of iron by plotting optical density against increasing amounts of the reagent, shows that the blue complex is formed when the ratio between the iron and the reagent is 1 : 1.

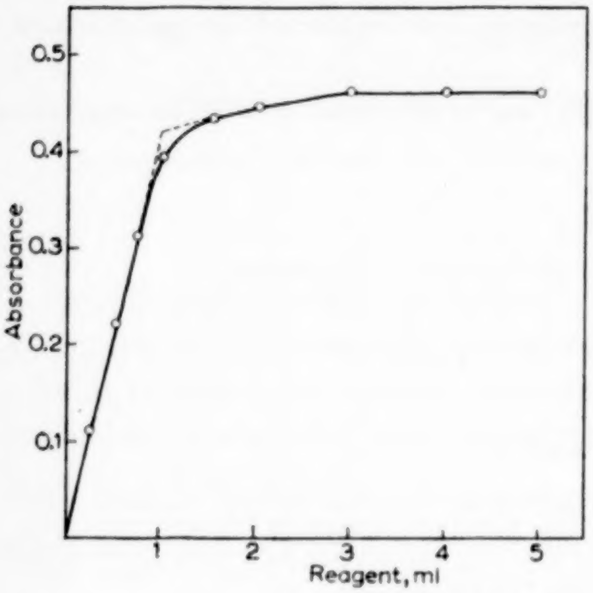


Fig.. 7. Molar ratio method.

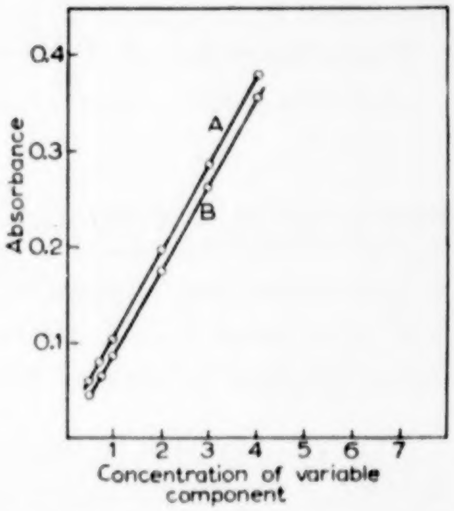
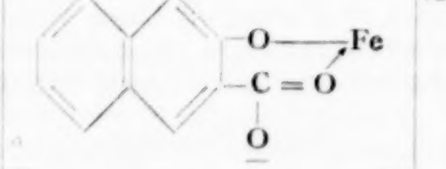


Fig. 8. Slope ratio method. A. reagent varying; B. Iron varying.

Confirmation of the above composition was provided by the slope ratio method and according to this, two series of solutions were prepared. In one series, the concentration of the reagent ($1.064 \cdot 10^{-3}M$) was varied in the presence of a constant excess of iron (5 ml of $5.32 \cdot 10^{-3}M$) and in the other, while the iron concentration ($1.064 \cdot 10^{-3}M$) was varied, the reagent was a constant component (5 ml of $5.32 \cdot 10^{-3}M$). The optical densities of the solutions were measured at the wavelength of the maximum absorption. The ratio of the slopes (Fig. 8) indicates a metal to reagent ratio of 1 : 1 in the complex.

In accordance with the views of WESP AND BORDE[8] regarding the complexes of ferric ion with phenolic derivatives and those of BENT AND FRENCH[9] and EDMONDS AND BIRNBAUM[10] for ferric thiocyanate complex, the composition of the soluble complex may be suggested to be $[Fe(C_{11}H_7O_3)]^{+2}$ while structurally it can be represented as



Extinction coefficient, degree of dissociation and instability constant

The molar extinction coefficient of the complex as calculated from Beer's law is 2212.

The degree of dissociation, a, has been calculated[11] from the relationship

$$a = \frac{E_m - E_s}{E_m},$$

where E_m is the maximum absorption of a given amount of iron in the presence of a large excess of the reagent used to ensure the complete complexing of the iron and E_s is the absorption of the same amount of iron mixed with a stoichiometric quantity of the reagent. From absorption measurements at 590 mμ, where the reagent had no absorption, the E_m and E_s were found to be equal to 0.396 and 0.3390 respectively at an iron concentration of $1.791 \cdot 10^{-4} M$. Therefore, the degree of dissociation, a, was equal to 0.1432.

From the value of a, the instability constant, K, is obtained from the equation

$$K = \frac{a^2 c}{1 - a},$$

where c is the concentration of the complex in moles per l. Therefore,

$$K = \frac{1.791 \cdot 10^{-4} \cdot (0.1432)^2}{0.8568} \quad \text{or} \quad K = 4.285 \cdot 10^{-4}$$

ACKNOWLEDGEMENTS

The authors wish to express their grateful thanks to the University Grants Commission, Government of India, for providing them with funds for the purchase of the Uvispeck Spectrophotometer and the Cambridge pH-indicator.

SUMMARY

2-Hydroxy-3-napthoic acid is presented as a new, highly sensitive and selective reagent for its colour reaction with ferric ion. The sensitivity of the reaction is 0.025 μg/cm² (SANDELL). The blue-coloured complex is maximally absorbed at 590 mμ and obeys Beer's law up to 24 p.p.m. of iron. The optimum range of concentration is from 4 to 20 p.p.m. of iron, where the percent relative analysis error per 1% absolute photometric error is 2.9. The composition of the complex, as evaluated by JOB's method and as verified by the Molar and Slope ratio methods, shows that in solution, the complex contains the iron and the reagent in a ratio of 1 : 1. The empirical formula of the complex is suggested to be $[\mathrm{Fe(C_{11}H_7O_3)}]^{+2}$. The molar extinction coefficient is 2212 and the instability constant of the complex is about $4.29 \cdot 10^{-4}$. Coloured ions or those ions that give coloured products are tolerated to a limited extent during the determination of iron.

RÉSUMÉ

L'acide hydroxy-2-naphtoïque-3 est proposé comme réactif sensible et sélectif pour le dosage du fer(III). La coloration bleue obtenue a une absorption maximum à 590 mμ et obéit à la loi de Beer pour des quantités de fer allant de 4 à 20 p.p.m. Les auteurs ont étudié également la constitution du composé formé.

ZUSAMMENFASSUNG

2-Hydroxy-3-naphtoesäure hat sich als ein empfindliches und selektives Reagens für die Bestimmung von Eisen-(III) erwiesen. Die erhaltene blaue Farbtönung besitzt ein Absorptionsmaximum bei 590 mμ; das Beer'sche Gesetz gilt für Konzentrationen von 4 bis 20 p.p.m. Es werden Angaben über die Struktur des erhaltenen Komplexes gemacht.

REFERENCES

[1] RUNGE, *Ann. Physik u. Chemie, Poggendorf's*, 31 (1834) 65.
[2] W. J. AGNEW, *Analyst*, 53 (1928) 30.
[3] K. DIETRICH AND K. SCHMITT, *Z. anal. Chem.*, 111(1937) 176.
[4] D. E. HOWE AND M. G. MELLON, *Ind. Eng. Chem., Anal. Ed.*, 12 (1940) 448.
[5] A. R. ARMSTRONG, *Dissertation*, University of Virginia, 1945.
[6] A. K. MAJUMDAR AND C. P. SAVARIAR, *Naturwissenschaften*, 4 (1958) 84.
[7] A. K. MAJUMDAR AND C. P. SAVARIAR, *Anal. Chim. Acta*, 21 (1959) 53.
[8] E. F. WESP AND W. R. BORDE, *J. Am. Chem. Soc.*, 56 (1934) 1037.
[9] H. E. BENT AND C. L. FRENCH, *J. Am. Chem. Soc.*, 63 (1941) 568.
[10] S. M. EDMONDS AND V. BIRNBAUM, *J. Am. Chem. Soc.*, 63 (1941) 1471.
[11] A. E. HARVEY, JR. AND D. L. MANNING, *J. Am. Chem. Soc.*, 72 (1950) 4488; 74 (1952) 4744

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SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH TIRON

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Sodium pyrocatechol disulphonate[1], disodium salt of 1,2-dihydroxybenzene-3,5-disulphonate, commercially known as Tiron, is a white crystalline compound highly soluble in water; its aqueous solution is stable for months. This reagent has been applied successfully for the colorimetric estimation of iron[2], titanium[3], molybdenum[4], cerium[5] and uranium[6].

In a neutral or alkaline medium, immediately on the addition of this reagent, copper forms a greenish-yellow complex and the sensitivity of its colour reaction is 2.5 p.p.m. of copper (0.24 μg/cm^2 according to SANDELL's definition) when measured at 375 mμ the region of maximum absorption. The complex adheres to Beer's law for a wide range of copper concentration, 10 to 160 p.p.m. of copper, and the ratio of metal to reagent in the complex as determined by Job's method[8] and confirmed by the method of molar ratio[2] is 1 : 2, with a dissociation constant on the order of $5.3 \cdot 10^{-6}$.

Ions of Fe^{+3}, Ti^{+4}, Ag^{+}, Au^{+3}, Nb^{+5}, Ta^{+5}, UO_2^{+2}, Ce^{+4}, MoO_4^{-2}, VO_3^{-}, CrO_4^{-2} and OsO_4 form coloured complexes and hence interfere in the determination of copper, but the ions of alkalis, alkaline and rare earths, Al^{+3}, Sn^{+4}, Zr^{+4}, Th^{+4}, Hg^{+2}, Pb^{+2} and WO_4^{-2} are tolerated when present in limited amounts.

EXPERIMENTAL

Apparatus and reagents

All absorption measurements were made with a U.V. Hilger's Spectrophotometer provided with a tungsten lamp, and quartz absorption cells of 1-cm light path. Corrections to compensate for the slight differences in the optical transmission of the cells were made whenever necessary.

pH measurements were made with a Cambridge pH indicator provided with an all-purpose glass electrode.

Standard copper solution

A standard solution of copper, containing 1 mg of copper per ml and having an acidity of 0.1 *N* in sulphuric acid, was prepared from an A. R. variety of crystallised copper sulphate and its strength was determined gravimetrically by α-benzoinoxime.

Solutions of other ions were prepared from their reagent-grade salts and the amount of ion present per ml of each solution was estimated by standard procedure.

Solutions of sodium acetate (5*N*) and sodium hydroxide (1*N*) were prepared from their salts of analytical variety.

The reagent 'Tiron' was prepared according to COUSIN's[1] method and was crystallised several times from hot water. A 25-g portion of the reagent was dissolved in 500 ml distilled water in order to prepare a 5% solution of the reagent and solutions weaker than this were obtained by proper dilution.

Spectral transmittancy

For transmittancy measurements, a few ml of the copper solution were taken in a 25-ml flask and diluted with water to make up the volume, after the addition, in succession, of 5 ml each of the reagent and the sodium acetate solutions. After colour appeared, the solution was placed in the absorption cell and its transmittancy in different wavelengths was measured against a reagent blank containing 1% Tiron in 1*N* sodium acetate solution. Curves 1 and 2 in Fig. 1 show the absorption of the copper–Tiron complex corresponding to 80 p.p.m. of copper against the reagent and water blanks respectively, and curve 3 shows the absorption due to the reagent blank only. The maximum absorption region for the complex thus appears to be at 375 mμ.

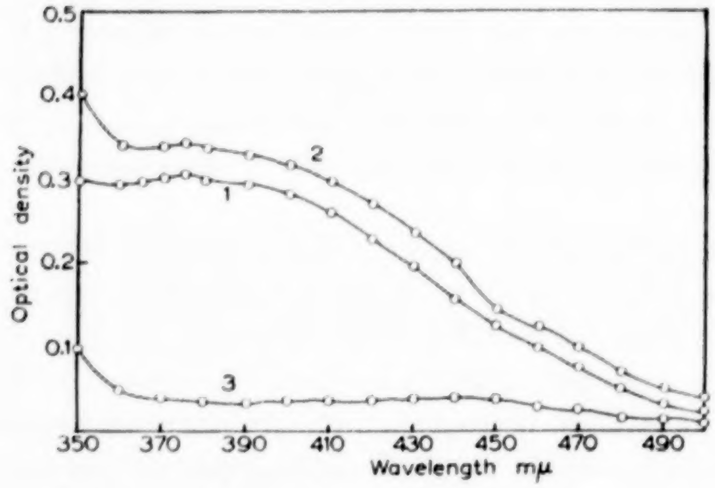

Fig. 1. Spectral transmittancy curves.

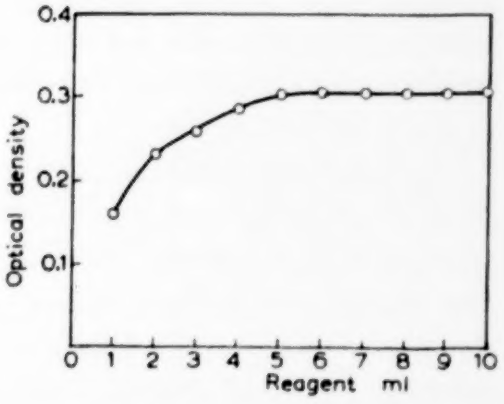

Fig. 2. Effect of reagent concentration.

Effect of reagent

Equal quantities of copper sulphate solution (80 p.p.m. of Cu) were taken separately in ten 25-ml flasks. Tiron solutions (5%) in different aliquots of 1 to 10 ml were added to each flask along with 5 ml of the sodium acetate solution. After making up the volume of each flask to 25 ml with distilled water, optical density of each solution was measured at 375 mμ against a water blank and each density measurement was corrected for the absorption due to the reagent. The curve in Fig. 2, representing the effect of the reagent, shows that when the reagent concentration is 1%, the intensity of the colour is maximal and remains so even with further amount of the reagent. Hence for subsequent work the concentration of the reagent was constantly maintained at 1%.

Effect of pH and time

At and above pH 8.0, the colour of the complex becomes deep yellow, and below pH 5.5, the full colour development does not take place. At a pH region of 6.1 to 6.9, the optical density was found to be always constant. Over pH 7.0, the shade changes with a shift of the maximum absorption to 430 mμ. Thus, for subsequent measurements the pH of the solution was kept at about 6.4 with sodium acetate.

The rate of reaction between copper and Tiron is instantaneous and the colour is stable for over 24 h. Though a negligible increase in intensity is observed in the first few hours, the intensity thereafter remains constant. Absorbancies, however, were measured immediately after mixing.

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Beer's law

Copper sulphate solution taken in a 25-ml flask was treated in succession with 5 ml of the Tiron solution (5%), 5 ml of sodium acetate, and a few drops of the sodium hydroxide solution for the adjustment of pH. The solution was made up to 25 ml with water and its absorption was measured at 375 mμ against a reagent blank. On plotting the density against the concentration of copper (Fig. 3) it is observed that the system adheres to Beer's law within 10 to 160 p.p.m. of copper.

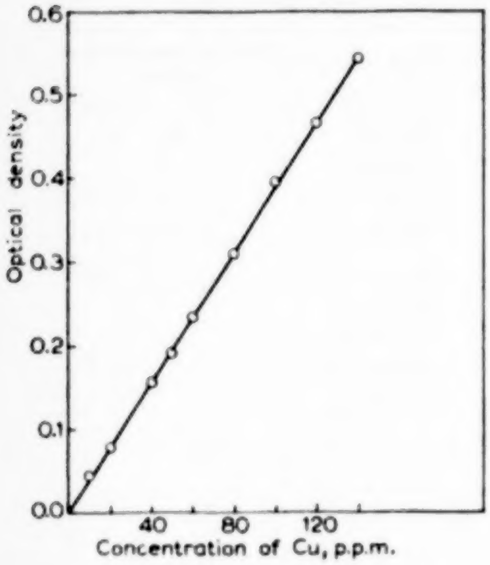


Fig. 3. Beer's law curve for copper–tiron complex.

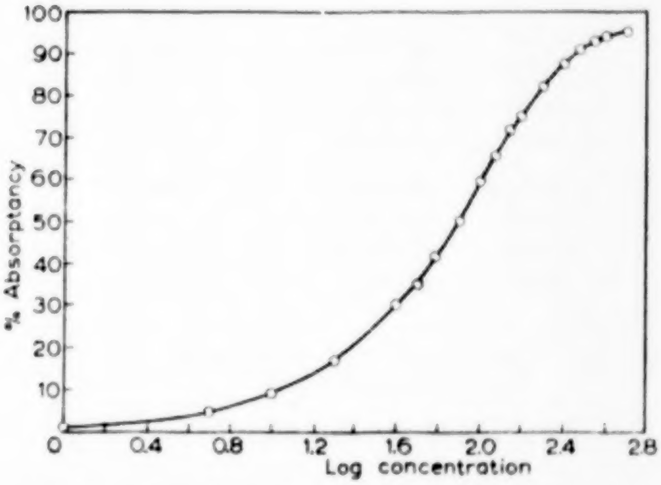


Fig. 4. Standard curve for copper–tiron complex.

Optimum range and accuracy

In order to define a suitable range and to evaluate the accuracy in photometric analysis, the percent absorbancy has been plotted as the ordinate against the logarithm of concentration as abscissa according to the proposal of RINGBOM[9]. It has been found that the optimum concentration range, as obtained from the slope of the curve (Fig. 4), is from 50 to 160 p.p.m. and for this range, the relative analysis error per 1% absolute photometric error as calculated from the equation[7] given below, is 2.94%.

$$\frac{\%\ \text{relative analysis error}}{1\%\ \text{absolute photometric error}} = \frac{230}{\mathrm{d}I/\mathrm{d}\log C}$$

Effect of diverse ions

The ions of Fe^{+3}, Ti^{+4}, Ce^{+4}, UO_2^{+2}, Nb^{+5}, Ta^{+5}, MoO_4^{-2}, CrO_4^{-2}, OsO_4, and VO_3^- yield colour reactions with the reagent. Au^{+3} and Ag^+ are reduced to the metallic state.

The ions of Ca^{+2}, Ba^{+2}, Sr^{+2}, Hg^{+2}, Pb^{+2}, Sn^{+2}, Sn^{+4}, Th^{+4}, Zr^{+4}, rare earths and WO_4^{-2} are found to form colourless complexes with no characteristic absorption in the visible region, though they consume some reagent and thus decrease the colour intensity of the copper–Tiron complex. Hence in the presence of a large excess of the reagent, these ions are tolerated to a limited extent.

For the study of the effect of the ions, copper sulphate solution (2 mg of copper) was taken in a flask along with the ion under investigation. 5 ml of the 5% reagent solution and 5 ml of the sodium acetate solution were added in succession, so as to adjust the pH to 6.4, and then water was added to make up the volume to 25 ml. The optical density of the solution was than measured against a reagent blank. An ion was considered to interfere if the resulting solution differed by 0.005 unit in optical density from that containing only copper and no diverse ions. Results are given in Table I.

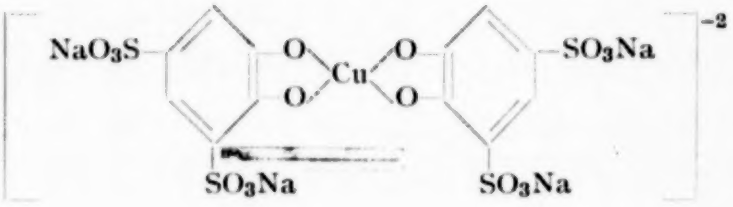
TABLE I

TOLERANCE TO DIVERSE IONS

Ion	*Added as*	*Limiting concentration p.p.m.*	*Ion*	*Added as*	*Limiting concentration p.p.m.*
Al^{+3}	$Al(NO_3)_3$	50	Mg^{+2}	$MgCl_2$	30
As^{+3}	$AsCl_3$	30	Mn^{+2}	$MnCl_2$	2
Be^{+2}	$BeCl_2$	5	Ni^{+2}	$Ni(NO_3)_2$	5
Bi^{+3}	$Bi(NO_3)_3$	6	Sb^{+3}	$SbCl_3$	10
BO_3^{-3}	H_3BO_3	10	Sn^{+2}	$SnCl_2$	5
Cd^{+2}	$Cd(NO_3)_2$	20	Sn^{+4}	$SnCl_4$	5
Co^{+2}	$Co(NO_3)_2$	4	Th^{+4}	$Th(NO_3)_4$	2
Hg^{+2}	$HgCl_2$	10	Zn^{+2}	$Zn(NO_3)_2$	15
			Zr^{+4}	$Zr(NO_3)_4$	5

Composition of the complex

The composition of the greenish-yellow soluble complex was studied by **Job**'s method[8] of continuous variation. Absorption due to mixtures (total volume kept constant) of equimolecular solutions at room temperature was measured at 375 mμ. The peak of the curve in Fig. 5, obtained by plotting the optical densities against increasing amounts of copper in complementary mixtures of copper and Tiron, indicates that the greenish-yellow complex has a composition in which the metal and the reagent are in a ratio of 1 : 2. The mole ratio method of **Yoe** *et al.*[2] gives the same ratio (curves not shown). The reagent being a bidentate ligand, the complex may be represented as



Dissociation constant

From the absorption data of the mixtures of non-equimolecular solutions (Fig. 6), the dissociation constant K has been calculated according to the equation (see ref.[10])

$$K = \frac{C^{m+n-1} \cdot p^{(n-1)} \cdot [(pm + n)x - n]^{m+n}}{m^{n-1} \cdot n^{(m-1)} \cdot (p - 1)^{m+n-1} [n - (m+n)x]}$$

where m and n are 1 and 2 respectively, C is the molar concentration of copper, pc is the molar concentration of Tiron, x equals ml of the Tiron solution combining with the $(1-x)$ ml of the copper giving the maximum effect.

The instability constant K has been found by substituting the values of x, p and c in the above equation as given in Table II.

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TABLE II

Fig.	*Curve*	*Concn. of copper*	*Concn. of Tiron*	*x*	*p*	*K*
6	1	$0.01 M$	$0.02 M$	0.54	2	$2.15 \cdot 10^{-6}$
6	2	$0.005 M$	$0.02 M$	0.42	4	$8.4 \cdot 10^{-6}$

Mean $K = 5.28 \cdot 10^{-6}$; the ionic strength is that of normal sodium acetate.

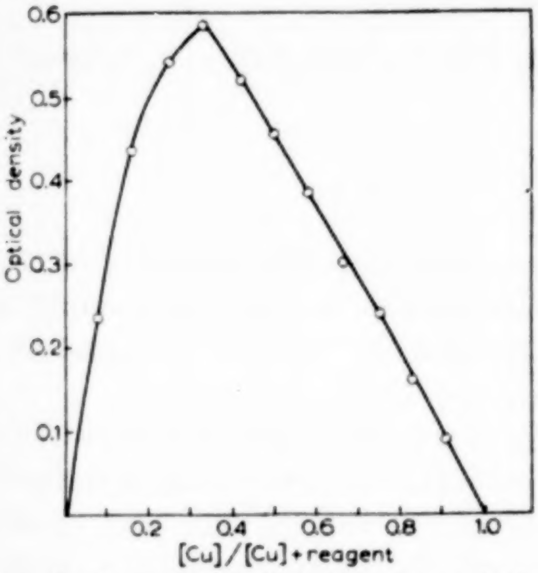

Fig. 5. JOB's method of continuous variation, $2 \cdot 10^{-2} M$ solutions.

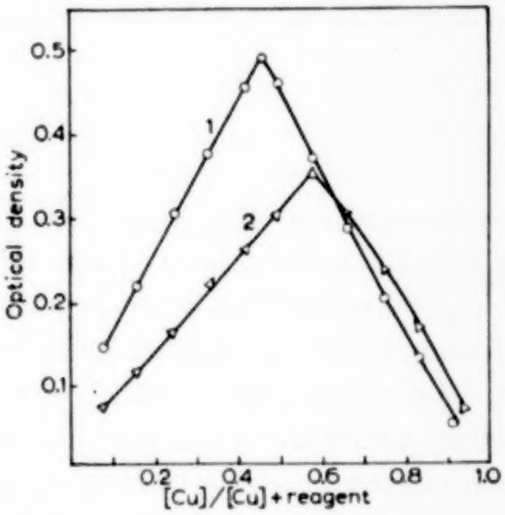

Fig. 6. Mixtures of non-equimolar solutions. (1) $2 \cdot 10^{-2} M$ reagent and $10^{-2} M$ Cu; (2) $2 \cdot 10^{-2} M$ reagent and $0.5 \cdot 10^{-2} M$ Cu.

SUMMARY

The reagent Tiron forms a soluble greenish-yellow complex with copper. The sensitivity of the colour reaction is 0.24 μg of copper/cm². The colour system at a pH of 6.1 to 6.9 is stable for over 24 h and shows a maximum absorption at 375 mμ. It obeys Beer's law at the latter wave length within a copper concentration of 10 to 160 p.p.m. The optimum range, however, is from 50 to 160 p.p.m. of copper, where the percent relative analysis error per 1% absolute photometric error is 2.94. JOB's method of continuous variation and the molar ratio method of YOE *et al.*[2] indicate that in solution the complex contains the metal and the reagent in a ratio of 1 : 2, with a dissociation constant on the order of $5.3 \cdot 10^{-6}$.

RÉSUMÉ

Le „tiron" est proposé comme réactif pour le dosage colorimétrique du cuivre. Il permet d'obtenir une coloration jaune verdâtre, stable, ayant une absorption maximum à 375 mμ.

ZUSAMMENFASSUNG

Zur colorimetrischen Bestimmung von Kupfer wird Tiron als Reagenz vorgeschlagen. Dieses bildet mit Kupfer einen stabilen, löslichen, grünlichgelb gefärbten Komplex, dessen Absorptionsmaximum bei 375 mμ liegt.

REFERENCES

[1] H. COUSIN, *Compt. rend.*, 117 (1893) 144; *Bull. soc. chim.*, 11 (1894) 104.
[2] J. H. YOE AND A. L. JONES, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 111.
[3] J. H. YOE AND A. R. ARMSTRONG, *Anal. Chem.*, 19 (1947) 100.
[4] W. FITZ AND J. H. YOE, *Anal. Chim. Acta*, 8 (1953) 546.
[5] B. SARMA, *J. Sci. Ind. Research (India)*, 15B (1956) 696.
[6] B. SARMA AND C. P. SAVARIAR, *J. Sci. Ind. Research (India)*, 16B (1957) 80.
[7] G. H. AYRES, *Anal. Chem.*, 21 (1949) 652.
[8] P. JOB, *Compt. rend.*, 180 (1925) 928; *Ann. chim. Paris*, 9 (1928) 113.
[9] A. RINGBOM, *Z. anal. Chem.*, 115 (1938) 332.
[10] A. K. MAJUMDAR AND B. SEM, *Anal. Chim. Acta*, 8 (1953) 369.

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THE DETERMINATION OF SMALL AMOUNTS OF TIN IN COPPER AND ITS ALLOYS

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INTRODUCTION

Until recently, analytical procedures for determining impurity amounts of tin in copper-base materials[1-12] have either been unsatisfactory or time consuming and the need existed for a simple rapid method, particularly for the examination of materials where specifications limit the tin content to 0.01%.

A qualitative test, in which phenylarsonic acid reacts with a solution of tin(IV) to produce a turbidity, has been published for the detection of 0.001% tin in analytical grade copper[13]. The 4-hydroxy-3-nitro derivative of this reagent was later used for determining tin in antimony sulphide[14] and, in 1956, this derivative was recommended for the determination of trace amounts of tin in refined copper[15], but no indication was given of the effect of impurities.

Over the past four years, these two reagents have been in regular use in our laboratories for the determination of tin in copper and copper alloys and, in view of the lack of published information on this subject, results of our experimental work are given in this contribution. The procedures described were developed for use with a Spekker absorptiometer because this instrument is in regular use in most control laboratories.

Part 1 of this paper describes the development of a turbidimetric procedure using phenylarsonic acid.

When iron is present above about 0.1%, an alternative procedure, using the 4-hydroxy-3-nitro derivative of phenylarsonic acid is necessary, and development of this procedure is described in Part 2.

PART 1 – USING PHENYLARSONIC ACID

Experimental

(*a*) *Preliminary tests*

It was established that a mixed hydrochloric–nitric acid solvent was preferable to the nitric acid (1 + 1) recommended for the qualitative test[13]. This mixed solvent enables higher amounts of tin to be determined because the resulting turbidity produced by the reagent is more finely dispersed whilst the limit of detection was about 0.001–0.002% on a 1-g sample. Transmission curves of solutions containing solvent, copper and tin were obtained using a Unicam spectrophotometer (S.P. 600). These tests indicated that an Ilford No. 601 filter was a convenient filter to use with a Spekker absorptiometer and all subsequent optical density measurements referred to in Part 1 were made with this instrument using a tungsten filament lamp, Ilford 601 filters and 1-cm cells.

(*b*) *Development of turbidity*

A tentative method was prepared and applied to 0.5-g samples of copper dissolved in 5 ml of a mixed hydrochloric–nitric acid solvent; varying amounts of a standard tin solution, covering the range 0.01 to 0.14% tin, were then added. The solutions were warmed to about 80° and to each was added 10 ml of an aqueous solution of phenylarsonic acid (5%). Each solution was cooled, the final volume was adjusted to 50 ml, and the optical density was determined after the turbidity had developed for 15, 30 and 60 min (Table I).

TABLE I

EFFECT OF STANDING TIME ON TURBIDITY

Tin added %	*Drum reading after:*		
	15 min	*30 min*	*60 min*
Nil	0.020	0.020	0.020
0.01	0.055	0.070	0.070
0.02	0.115	0.135	0.130
0.04	0.195	0.185	0.175
0.06	0.290	0.275	0.260
0.10	0.495	0.430	0.390
0.14	0.515	0.335[a]	0.335[a]

[a] Precipitate appeared

Although limited in number, these tests indicate that when the tin content does not exceed about 0.02%, a time interval of about 30 min is essential in order to ensure maximum development of the turbidity. Where tin up to 0.1% is present, it is essential to standardize the standing period and a time interval of 30 min was chosen as a convenient compromise. Based on this information a tentative procedure *(A)* was prepared and a calibration curve was constructed as detailed in the Appendix.

(*c*) *Effect of other elements*

Reagents containing the phenylarsonic group react preferentially with quadrivalent metals, particularly thorium, tin, titanium and zirconium[16]. Other metals, *e.g.* cerium(IV), hafnium, tungsten(VI) and uranium, yield insoluble compounds but none of these less common elements occurs in normal copper-base alloys. Iron(III), however, partly precipitates under these conditions and its effect, together with the effects of other metals likely to be encountered, was investigated.

Tests on a brass sample, reputed to contain 0.075% tin, indicated that zinc up to 40% and lead up to 2%, caused no interference. Further experiments were made in which iron and various other elements were added to a solution of the same brass sample; results of these tests are summarised in Table II.

Conclusions reached from the results shown in Table II are that, of the elements investigated, silicon and tellurium, in amounts normally present in copper-base materials, will only have a slight tendency to cause low results, but interference by iron is serious.

Attempts were made to overcome the effect of iron, and reagents such as citric, tartaric, phosphoric, hydrofluoric acid and/or ethylenediaminetetracetic acid were

TABLE II

EFFECT OF OTHER ELEMENTS

Element added:	—	Al[a]	Ni[a]	Mn[b]	Se[b]	Si[b]	Te[b]	Fe%	0.2	0.5	1.0	2.0	10.0
Tin (%) found:	0.075	0.071	0.071	0.076	0.074	0.060	0.064		0.064	0.018	0.009	0.009	0.002

Equivalent to [a] 10%, [b] 5%

all tried but none was entirely satisfactory. It was established by further experiments that, provided the iron and tin contents of the sample did not individually exceed about 0.06%, application of the tentative procedure is reliable. When tin exceeded 0.06%, lower sample weights were taken (see Appendix, *method A*, *Note 1*) and in this way, tin up to 0.4% could be determined with reasonable accuracy provided that the amount of iron present did not exceed the tin content of the sample.

Application of method to typical samples

Method A was applied to a selection of copper-base alloys and results obtained (Table III), are in reasonable agreement with results obtained by an alternative volumetric procedure based on a preliminary separation of tin as hydroxide, in the presence of added iron, reduction with hypophosphite and titration of the stannous solution with a standard potassium iodate–iodide solution[8,9].

TABLE III

RESULTS ON TYPICAL SAMPLES

Alloy	*Tin (%)*	
	(Turbidimetric procedure method A)	*Volumetric procedure*
Brass 70/30 Cu/Zn	0.035 0.035	0.03
	0.035 0.035	0.03
	0.11 0.10	0.09
Leady brass (1.5% Pb)	0.33 0.30, 0.30	0.31
	0.26 0.23, 0.24	0.25
	0.15 0.14	0.14
	0.49 0.53	0.53
Leady brass (2.5% Pb)	0.20 0.22, 0.22	0.21
	0.29 0.28	0.28
	0.34 0.34	0.35
	0.46 0.48	0.44

The turbidimetric method is simple and rapid but the serious limitations imposed when iron is present, necessitated further experimental work and this is described in Part 2.

PART 2 – USING 4-HYDROXY-3-NITRO-PHENYLARSONIC ACID

Experimental

(*a*) *Preliminary tests*

Iron is an important constituent of several copper-base alloys, *e.g.* D.T.D. 197, specifies 4–6% iron, and limiting values for tin may be as low as 0.015%.

Because the 4-hydroxy-3-nitro derivative of phenylarsonic acid, subsequently referred to as 4H-3N-PA, is stated to offer advantages over the parent reagent, particularly in the presence of iron[14], use of this reagent was investigated. In the following experiments the final turbidity was developed in a dilute sulphuric acid solution because chlorides are known to interfere in the reaction[14].

Preliminary tests indicated that an acidity equivalent to about 2 ml of conc. sulphuric acid/50 ml was necessary in order to prevent precipitation of the ron–4H-3N-PA complex. Higher acidities were equally effective for this purpose, but formation of the tin–4H-3N-PA complex was delayed and a solution of minimum acidity was desirable. In the examination of copper-base samples a suitable acidity was obtained by dissolving 0.5 g of the sample in 10 ml of a nitric–sulphuric acid mixture; nitric acid was subsequently removed by evaporation. These experiments indicated that 4H-3N-PA was more sensitive than the parent phenylarsonic acid and tests on the limit of detection are detailed later.

Transmission–wavelength curves were prepared, using a Unicam spectrophotometer (S.P. 600), and it was shown that the reagent, in a sulphuric acid solution containing copper only, had negligible absorption over the wave-length range 4600–5000 Å; in the presence of tin, maximum absorption occurred at 4700 Å.

Using the tentative procedure (*B*) and a Spekker absorptiometer (tungsten filament lamp), Ilford 602 filter and 1-cm cells, a calibration graph covering the range 0.01–0.06% tin was prepared.

(*b*) *Effect of iron*

Initial experiments indicated that iron up to 0.25% had no significant effect on the determination. With higher amounts of iron, up to 1.5%, the standing period had to be increased from 30 to 90 min in order to obtain full development of the turbidity.

TABLE IV

EFFECT OF IRON

Total iron present %	*Tin (%) after standing for*		
	90 min	*3 h*	*20 h (Overnight)*
1.6	0.030	0.031	—
2.6	0.025	0.027	—
3.6	0.019	0.024	0.031
5.1	0.015	0.020	0.028
6.6	0.011	0.013	0.026

Further tests were made on solutions containing 0.5 g of a copper–nickel–iron alloy (0.03% tin and 1.6% iron) to which various additions of iron were made. Results obtained are summarised in Table IV.

These results indicate that maximum turbidity is obtained after about 3 h provided the iron content does not exceed about 2.0%. In the examination of samples containing iron in excess of this amount formation of the turbidity was incomplete and precipitation occurred. In subsequent tests, where iron exceeded 2.0%, the tin complex was allowed to settle overnight, it was then filtered, ignited, dissolved and examined for tin as in the absence of iron. Details of this modification are given in *Method C* and the results obtained on typical samples (Table V) are in reasonable agreement with those obtained by the volumetric method[8,9].

(*c*) *Effect of other elements*

Various additions were made to solutions containing 0.5 g of copper and the equivalent of 0.03% of tin and it was shown that the following elements had no significant effect in the determination.

TABLE V

RESULTS ON SAMPLES CONTAINING IRON, USING THE MODIFIED PROCEDURE

Iron present %	*Tin (%)*	
	Volumetric procedure	*Proposed procedure (method C)*
4–6	0.025	0.026
4–6	0.023	0.022
4–6	0.023	0.018
4–6	0.060	0.061
4–6	0.032	0.036
11.6	0.030	0.027
11.6	0.030	0.025
6.6	0.030	0.027

Aluminium (10%), antimony (0.10%), arsenic (10%), bismuth (1.0%), cadmium (10%), chromium (0.5%), lead (5%), nickel (10%), phosphorus (1%), selenium (5%), silicon (5%) and tellurium (1%).

Lead and silicon had no effect providing they were removed by filtration, after fuming with sulphuric acid. Antimony above 0.1% and up to 1% did not interfere, provided 1 g of tartaric acid was added before addition of the reagent. Reference has been made to the possible presence of tin oxide in copper[17] and although no evidence of oxide has been encountered, provision for this eventuality is made in the method.

(*d*) *Limit of detection*

Using 2 g of electrolytic copper and known additions of tin, it was found that the limit of detection of tin was about 0.0002%. The slight modification required for this increased weight is detailed in *Method D*.

Application of 4-hydroxy-3-nitro-phenylarsonic acid method

The proposed *Method B* was applied to 6 independent samples of copper–nickel–iron alloys, each containing about 1.5% iron and under 0.05% tin. Results (Table VI) obtained by two analysts, are in close agreement with those obtained by the volumetric procedure[8,9].

TABLE VI

COMPARISON OF VOLUMETRIC AND TURBIDIMETRIC METHODS

Tin (%)			
Volumetric procedure	*Proposed procedure (method B)*		
	Analyst A	*Analyst B*	
0.020	0.018	0.019	0.020
0.024	0.025	0.027	0.027
0.020	0.017	0.019	0.019
0.020	0.018	0.021	0.020
0.029	0.031	0.033	0.033
0.039	0.037	0.037	0.039

Similar agreement between the two methods was obtained on two samples of brass containing about 2.5% of lead and about 0.4% of tin.

Further tests were made on a sample of brass (copper 58%, lead 3%, and iron 0.25%). Six determinations on aliquots from a stock solution gave results ranging between 0.275 and 0.290% tin. Four tests on independently weighed samples of the same material gave results of 0.285, 0.290, 0.270 and 0.275% tin compared with a single value of 0.29% obtained by the alternative volumetric procedure.

Method D, for application when tin is below 0.01%, was applied to nine samples of pure brass (copper 70%, zinc 30%) and results obtained (Table VII) were in good agreement with those obtained by the volumetric procedure.

TABLE VII

Sample	*Tin (%)*	
	Proposed procedure (method D)	*Volumetric procedure*
A	0.0015	0.001
B	0.0055	0.005
C	0.003	0.003
D	0.002	0.0015
E	0.0015	0.0015
F	0.0025	0.002
G	0.0035	0.004
H	0.003	0.003
I	0.006	0.0065

CONCLUSIONS

Compared with other known procedures for determining tin in copper-base materials, the proposed procedures are quicker, simpler and sufficiently accurate for determining tin up to about 0.4%.

Of the two recommended turbidimetric methods, the phenylarsonic acid method is the more rapid but it is less sensitive and, without modification, is limited in its application to samples containing under 0.1% iron. With this exception, usual impurities and alloying metals, normally associated with copper and its alloys, do not interfere. This method is, therefore, particularly useful for use in routine control laboratories.

The procedures, using 4H-3N-PA are more time consuming but are applicable in the presence of alloying amounts of iron and are recommended for the examination of typical copper-base materials.

The higher sensitivity of the 4H-3N-PA derivative offers distinct advantages for the determination of trace amounts of tin. On a 2-g sample, tin as low as 0.0002% can be detected and tin in excess of 0.001% can be determined accurately and rapidly. Fourteen samples containing 0.001–0.006% tin can be completed in about six hours, whereas other methods take considerably longer and are more difficult to apply, particularly in the examination of complex copper alloys containing appreciable amounts of iron, aluminium and manganese, *e.g.* D.T.D. 197 alloys.

The recommended procedures have now been in use in our routine laboratories for about four years and over this period a satisfactory order of reproducibility and accuracy has been maintained. Selectivity of the reagents and the relative simplicity of the methods suggest wider applications, provided metals which produce turbidities under similar conditions, *e.g.* titanium and zirconium, are absent.

ACKNOWLEDGEMENT

We thank Mr. W. T. ELWELL for helpful suggestions in the preparation of this paper.

APPENDIX

METHODS FOR THE TURBIDIMETRIC DETERMINATION OF TIN IN COPPER ALLOYS

Method using phenylarsonic acid

Method A: For tin contents 0.01–0.4% (iron not exceeding 0.06%) – Note 1

Reagents

Nitric–hydrochloric acid mixture. To 50 ml of water add 32 ml of nitric acid (d = 1.42) and 12 ml of hydrochloric acid (d = 1.18). Cool and dilute to 100 ml.

Phenylarsonic acid solution (5%) Dissolve 5 g of phenylarsonic acid in warm water and dilute to 100 ml. This reagent must be freshly prepared and filtered before use.

Standard tin solution. Weigh the calculated amount of a bronze, of known tin content (about 10%), so that the sample contains 10.0 mg of tin. Dissolve in 5 ml of nitric–hydrochloric acid mixture and dilute to 100 ml. (1 ml contains 0.1 mg tin) This solution must be freshly prepared.

Preparation of calibration graph

Transfer 0.5 g of pure copper (tin free) to each of six 150-ml. beakers, add 5 ml of nitric–hydrochloric acid mixture and heat gently until the metal has dissolved. Cool and add separately 0.5, 1.0, 2.0, 3.0 and 4.0 ml of the standard tin solution (1 ml = 0.1 mg tin) to five of the copper solutions; use the remaining solution as a blank on the reagents.

Proceed with each as follows: Dilute to 30 ml, heat to boiling, remove from the source of heat and add immediately 10 ml of phenylarsonic acid solution (5%) (heated to 80°). Cool to 20° and dilute to 50 ml in a calibrated flask. Allow to stand for 30 min, shake the flask, then measure the optical density at a wavelength of 4200 Å. For measurements on a Spekker absorptiometer use a tungsten filament lamp, 1-cm cell and Ilford 601 filters.

Correct for the blank and prepare a calibration graph.

Procedure

Transfer 0.5 g of sample (*Note 1*) to a 150-ml beaker. As a blank on the reagents used, transfer a similar weight of copper (tin free) to a 150-ml beaker and proceed as for the examination of the sample. Add 5 ml of the nitric–hydrochloric acid mixture, and heat gently until the metal has dissolved. (*Note 2*). Adjust the volume of the

TABLE VIII

Sample weight g	*Tin content* %	*Maximum iron permissible* %
0.5	0.01–0.06	0.06
0.2	0.05–0.15	0.15
0.1	0.10–0.30	0.30
0.05	0.20–0.4	0.40

solution to about 30 ml and continue as described for the preparation of the calibration graph *(Note 3)*. Correct for the blank value and calculate the tin content of the sample by reference to the calibration graph.

Notes

1. If the tin content is above 0.05%, a lower sample weight must be used. The maximum permissible iron content is then increased (Table VIII).

2. If a residue is observed, filter the solution through a close texture filter-paper and wash with warm water. Calcine the paper and insoluble matter in a silica crucible and cool. Fuse the residue in 0.5 g of potassium bisulphate, cool, dissolve in 10 ml of hydrochloric acid (1 + 10), add the solution to the filtrate and proceed as recommended.

3. If the optical density exceeds 0.50, repeat the determination using a smaller sample weight. Excessive amounts of tin may lead to partial deposition of the complex and cause low results.

Methods using 4-hydroxy-3-nitro-phenylarsonic acid

Method B: For tin contents 0.01–0.4% tin (iron not exceeding 2.0%) – Note 1

Reagents

Nitric–sulphuric acid mixture. To 110 ml of water add 50 ml of nitric acid ($d = 1.42$) and 40 ml of sulphuric acid ($d = 1.84$).

4-Hydroxy-3-nitro-phenylarsonic acid reagent (4H-3N-PA) (2%). Dissolve 2 g of the reagent in 30 ml of methyl alcohol and dilute with water to 100 ml. This reagent must be freshly prepared and if necessary filtered before use.

Standard tin solution. As for ***method A***.

Preparation of calibration graph

Transfer 0.5 g of pure copper (tin free) to each of seven 150-ml beakers, add 15 ml of nitric–sulphuric acid mixture and heat gently until the metal has dissolved. Cool and add separately 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ml of the standard tin solution (1 ml = 0.1 mg tin) to six of the copper solutions, use the remaining solution as a blank on the reagents. Proceed with each solution as follows:

Evaporate until white fumes of sulphur trioxide appear, cool, wash down the side of beaker with 20 ml of water and heat until solution of salts is complete. Cool to 20°, add 10 ml of the 4H-3N-PA solution (2%) and dilute to 50 ml in a calibrated flask. Allow to stand for 30 min, shake the flask and then measure the optical density at a wavelength of 4700 Å. For measurements on a Spekker absorptiometer use a tungsten lamp, 1-cm cell and Ilford 602 filters.

Correct for the blank value and prepare a calibration graph.

Procedure

Transfer 0.5 g of sample to a 150-ml beaker *(Note 1)*. To provide a blank on the reagents used, transfer a similar weight of pure copper (tin free) to a 150-ml beaker and proceed as for examination of the sample. Add 15 ml of nitric–sulphuric acid mixture and heat gently until the metal has dissolved *(Note 2)*. Evaporate until white fumes of sulphur trioxide appear, cool, wash the side of the beaker and cover with 20 ml of water and heat gently until all salts have dissolved *(Note 3)*. Cool, add 10 ml of the 4H-3N-PA solution (2%) and then proceed as described for preparation of the calibration graph. *(Notes 4 and 5)*.

Correct for the blank value and calculate the tin content of the sample by reference to calibration graph.

Notes

1. This sample weight is recommended for tin contents 0.01 to 0.03%. For higher percentages of tin a smaller weight of sample must be taken and the amount of solvent reduced (see Table IX).

TABLE IX

Tin content %	*Sample weight* ml	*Solvent acid* g
0.01 –0.03	0.5	10
0.025–0.08	0.2	8
0.05 –0.16	0.1	7
0.10 –0.30	0.05	7
0.20 –0.40	0.03	7

Where a sample weight of less than 0.5 g is taken, a higher iron content can be tolerated *e.g.* 5% iron on the 0.2-g sample and 10% for the lower weights.

For accurate determinations of 0.01–0.03% tin, the maximum iron permissible is restricted to 2.0% but this limit can be extended to 2.5% for routine determinations.

2. See *method A, Note 2*, but on this occasion dissolve the cooled bisulphate melt in 10 ml of sulphuric acid (1 + 99) and add the extract to the filtrate.
3. If lead or silicon is present, allow the solution to cool, filter off lead sulphate and/or silica on a close texture filter paper and wash with sulphuric acid (1 + 99). Evaporate the filtrate to 30 ml and continue as described in the procedure.
4. In the presence of iron in excess of 0.25%, up to 1.5%, allow to stand for 90 min before determining the optical density. In the presence of 1.5–2.0% iron (up to 2.5% for routine tests) allow to stand for 3 h. If the iron content is unknown, the optical density must be determined after 30, 90 min and 3 h. If the value is still increasing after 3 h then *Method C* must be used. If the iron content does not exceed about 1.5%, the minimum limit for tin is about 0.005%.
5. See *Method A, Note 3*, page 65.

Method C: For tin contents 0.01–0.03% (iron above 2.0%), e.g. D.T.D. 197 alloy

Use *Method B* up to the addition of the 10 ml of 4H-3N-PA solution (2%) then mix and allow the solution to stand overnight. Filter the precipitate, which consists of the tin complex and a small portion of iron, on to a close texture filter paper and wash with water. Transfer paper and precipitate to a silica crucible and calcine. Fuse in 2 g of potassium bisulphate and cool. Extract with water and transfer to a 150-ml beaker. Add 2 ml of sulphuric acid (*d*-1.84) and heat gently. Cool, add 10 ml of the 4H-3N-PA (2%) solution and proceed as described for the preparation of the calibration graph (*Method B*).

Correct for the blank value and calculate the tin content by reference to the calibration graph.

Method D: For tin 0.001–0.01% in copper (maximum iron 0.05%)

Reagents. As *Method B*

Preparation of calibration graph

Transfer 2 g of pure copper (tin free) to each of six 150-ml beakers, add 20 ml of the nitric–sulphuric acid mixture and heat gently until the metal has dissolved. Cool and add separately 0.5, 1.0, 1.5, 2.0 and 2.5 ml of the standard tin solution (1 ml = 0.10 mg tin) to five of the copper solutions; use the remaining solution as a blank. Proceed with each solution as described under "*Preparation of calibration graph*" (*Method B*, p. 65).

Procedure

Transfer 2 g of sample to a 150-ml beaker. As a blank on reagents transfer a similar weight of pure copper (tin free) to a 150-ml beaker and proceed as for the examination of the sample. Add 20 ml of the nitric–sulphuric acid mixture and heat gently until the metal has dissolved. Examine the solution for any insoluble residue *(Method B, Note 2)*. Evaporate the combined solutions until white fumes of sulphur trioxide appear, then proceed as described for preparation of the calibration graph.

Correct for the blank value and calculate the tin content of the sample by reference to the calibration graph.

SUMMARY

Turbidimetric procedures are recommended for the determination of tin, over the range 0.001–0.4%, in copper-base materials. Compared with other known methods, these procedures are simpler and invariably quicker. The procedure using phenylarsonic acid is applicable provided the amount of iron in the sample does not exceed the amount of tin to be determined. In the examination of samples containing alloying amounts of iron and small amounts of tin, the use of a more sensitive reagent 4-hydroxy-3-nitro-phenylarsonic acid, is recommended particularly for the determination of tin below 0.01%. With the exception of iron both procedures are relatively free from interference by common alloying elements.

RÉSUMÉ

Des procédés simples et rapides sont proposés pour le dosage turbidimétrique de l'étain, dans des alliages à base de cuivre, au moyen de l'acide phénylarsonique. Lors de faibles teneurs en étain ($< 0.01\%$), on recommande l'emploi de l'acide hydroxy-4-nitro-3-phénylarsonique.

ZUSAMMENFASSUNG

Es werden einfache und rasche Methoden beschrieben zur turbidimetrischen Bestimmung von Zinn in Kupferlegierungen mit Hilfe von Phenylarsinsäure. Bei sehr kleinen Zinnmengen($< 0.01\%$) wird die Verwendung von 4-Hydroxy-3-nitrophenylarsinsäure empfohlen.

REFERENCES

[1] J. W. Mellor, *A Treatise on Quantitative Inorganic Analysis*, Vol. 1, C. Griffin and Co., London, 1913, p. 308.

[2] W. W. Scott, *Standard Methods of Chemical Analysis*, Vol. 2, 5th Ed., The Technical Press Ltd., London, 1939, p. 1363.

[3] G. E. F. Lundell and J. I. Hoffman, *Outlines of Methods of Chemical Analysis*, J. Wiley, New York, 1945, pp. 47 and 210.

[4] A. Meyer, *Chem. Ztg.*, 46 (1922) 209.

[5] O. Gates and L. Silverman, *Ind. Eng. Chem., Anal. Ed.*, 11 (1939) 370.

[6] W. R. Schoeller and H. Holness, *Analyst*, 71 (1946) 217.

[7] J. S. Knapper, K. A. Craig and G. C. Chandlee, *J. Am. Chem. Soc.*, 55 (1933) 3945.

[8] W. J. Bayley, *Chem. & Ind. (London)*, (1950) 314.

[9] *Methods for the Analysis of Raw Copper*, (B.S. 1800), British Standards Institution, London, 1951, p. 40.

[10] J. I. Hoffman and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, 22 (1939) 465.

[11] W. D. J. Mogerman, *J. Research Natl. Bur. Standards*, 33 (1944) 307.

[12] E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 2nd. Ed., Interscience Publishers Inc., New York, 1950, p. 565.

[13] Anon., *AnalaR Standards for Laboratory Chemicals*, 3rd Ed., British Drug Houses Ltd., and Hopkin and Williams Ltd., London, 1944, p. 60.

[14] P. Karsten, H. F. Kies and J. J. Walraven, *Anal. Chim. Acta*, 7 (1952) 355.

[15] C. M. Dozinel and H. Gill, *Chemist Analyst*, 45 (1956) 105.

[16] J. F. Flagg, *Organic Reagents Used in Gravimetric and Volumetric Analysis*, Vol. IV, Interscience Publishers, Inc., New York, 1948, p. 107.

[17] W. E. Alkins and A. P. C. Hallowes, *J. Inst. Metals*, 54 (1) (1935) 125.

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NON-AQUEOUS DETERMINATION OF INORGANIC SALTS

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The procedures available for determination of salts in nonaqueous solutions are mostly limited to analysis of amine salts and to salts of the alkali and alkaline earth metals. Little information is available on nonaqueous titration of other inorganic salts, particularly salts of strong acids and strong bases.

KOLLING[1] reviewed the literature on methods proposed for volumetric analysis of inorganic compounds in nonaqueous solutions through early 1956.

There are a number of limitations to the analysis of salts by titration with perchloric acid. Many inorganic salts that would behave as bases in acetic acid are insoluble in this solvent, many salts form gelatinous precipitates during the titration, and it is not possible to differentiate the salt being analyzed from carbonate or hydroxide impurity. Several of these limitations also apply to those methods suggested for analysis of acidic salts by titr[illegible]n with alkali methoxides.

One technique commonly employed for determination of salts of organic bases and acids is to liberate the base with an excess of alkali or the acid with an appropriate mineral acid, extract with a nonaqueous solvent, and subsequently titrate the isolated base with perchloric acid, or the acid with alkali methoxide[2].

The extraction technique was modified to eliminate its laborious and time-consuming features, and its applicability for salt analysis was extended by combining acidification with a strong acid, a simple extraction, and a differentiating titration with tetrabutylammonium hydroxide.

PRINCIPLE OF METHOD

In a previous study[3], it was shown that strong monobasic acids can be titrated differentially in the presence of polybasic acids. This suggested that it should be possible to determine salts somewhat similarly — namely, acidify the salt with an excess of sulfuric acid and differentially titrate the liberated acid and the amount of sulfuric acid which was not required to react with the cationic portion of the test sample. The cation is precipitated as the sulfate by addition of a nonaqueous solvent. Thereafter, the determination is equivalent to the differentiating titration of the two acids, the liberated and added.

PROCEDURE

The apparatus and preparation of reagent have been described previously[4,5]. Accurately weigh 0.5 mequiv. of salt into a 100-ml volumetric flask. Dissolve the salt in 1 ml of water and 2 ml of 1*N* sulfuric acid. Add up to 3 additional ml of water if necessary to affect solution. Dilute to volume with either pyridine or acetone, stopper, and shake vigorously. Titrate a 50-ml aliquot of the supernatant of the dilution potentiometrically with $0.1N$ tetrabutylammonium hydroxide, and determine the end-points from a plot of the volume of titrant *versus* millivoltage. Substract the solvent blank from the final end-point.

Two or more inflections are obtained in the potentiometric curve. In some instances a separate inflection or inflections are obtained for the acid liberated from the salt; in others the acid or one of the acid equivalents may titrate with either the first or second equivalent of the residual sulfuric acid. The volume of titrant for the desired salt is ascertained by difference in all cases.

EXPERIMENTAL

Analysis of high purity salts

In order to prove the procedure analytically correct, samples of high purity sodium oxalate and sodium nitrate were analyzed. The salts were dissolved in water, excess sulfuric acid was added which yielded solutions containing oxalic acid, sulfuric acid and sodium sulfate, and nitric acid, sulfuric acid and sodium sulfate, respectively. Addition of a nonaqueous solvent precipitated the sodium sulfate, and the oxalic–sulfuric acid, and nitric–sulfuric acid mixtures were resolved by differentiating titrations on aliquots of the supernatant. Fig. 1 illustrates the potentiometric curves for these titrations. The oxalic-sulfuric acid titrations were performed in acetone, the nitric–sulfuric acid titrations in pyridine. In the oxalic–sulfuric acid potentiometric curve, the first and third inflections represent neutralization of the two sulfuric acid equivs., the second and fourth, the two oxalic acid equivs. On ten analyses of sodium oxalate, a mean value of 99.80% was realized with a standard deviation

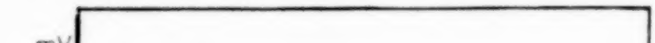

Fig. 1. Titration of sodium oxalate, (1), and sodium nitrate, (2), after acidification with sulfuric acid.

of 0.18. On ten analyses of sodium nitrate, a mean value of 99.60% was realized with a standard deviation of 0.31.

Analysis of representative salts

Table I lists a number of additional salts which were analyzed by this procedure. All salts were C.P. grade or better.

TABLE I

DETERMINATION OF SALTS BY ACIDIFICATION AND NONAQUEOUS TITRATION

Salt	*% Purity*	*Solvent*	*Number of inflections in potentiometric curve*
Sodium phosphate, dibasic ($Na_2HPO_4 \cdot 7H_2O$)	100.0 100.3	Acetone	3
Sodium phosphate, tribasic ($Na_3PO_4 \cdot 12H_2O$)	96.2 96.0	Pyridine	3
Sodium ammonium phosphate ($NaNH_4HPO_4 \cdot 4H_2O$)	99.5 98.9	Pyridine	3
Sodium phosphite ($Na_2HPO_3 \cdot 5H_2O$)	100.5 100.0	Acetone	5
Sodium chloride	97.2 97.3	Pyridine	2
Sodium bromide	99.4 99.2	Pyridine	2
Sodium nitrite	95.0 94.5	Pyridine	3
Potassium dichromate	99.0 98.5	Pyridine	2
Potassium chromate	97.2 97.3	Pyridine	2
Cupric acetate	100.1 100.9	Acetone	2
Nickel acetate	99.8 100.3	Acetone	2
Uranium acetate ($(UO_2)(C_2H_3O_2)_2 \cdot 2H_2O$)	98.3 99.3	Pyridine	2
Potassium hydrogen phthalate	100.1 99.9	Pyridine Acetone	3 4
Sodium potassium tartrate ($NaKC_4H_4O_6 \cdot 4H_2O$)	99.0 99.5	Pyridine Acetone	3 3
Sodium citrate	99.0 98.9	Pyridine Acetone	4 4
Sodium perchlorate	97.2 97.5	Pyridine	2
Sodium chlorate	98.5 99.2	Pyridine	2
Uranyl zinc acetate ($UO_2(C_2H_3O_2)_2 \cdot 2Zn(C_2H_3O_2)_2 \cdot 2H_2O$)	99.1 99.5	Pyridine	2

The curves for some of the potentiometric titrations listed in Table I are shown in Figs. 2, 3, 4. The curve for sodium nitrate, sulfuric acid, illustrated in Fig. 1, typifies the titration of a strong monobasic acid and sulfuric acid; whereas, the curve for uranium acetate, sulfuric acid, illustrated in Fig. 2, typifies the titration of a weak monobasic acid and sulfuric acid. In the latter titration, the first inflection represents neutralization of the first equivalent of sulfuric acid, the second represents neutralization of the second sulfuric and the acetic equivalents. The curves for the phosphate salts with sulfuric acid are all similar to that given for trisodium phosphate, sulfuric acid in Fig. 2. In this curve, the first inflection represents neutralization of the sulfuric acid equivalent, the second represents neutralization of the second sulfuric acid and the first phosphoric acid equivalents, the third represents neutralization of the second phosphoric acid equivalent. The titration of sodium potassium tartrate, sulfuric acid in pyridine and of potassium hydrogen phthalate, sulfuric acid in acetone are illustrated in Fig. 3. In the first curve, the first inflection represents neutralization of the first sulfuric acid equivalent, the second, the first tartaric acid equivalent, the third represents neutralization of the second sulfuric acid and tartaric acid equivalents. In the second curve, the first and third inflections represent neutralization of the two sulfuric acid equivalents, the second and fourth, the two phthallic acid equivalents.

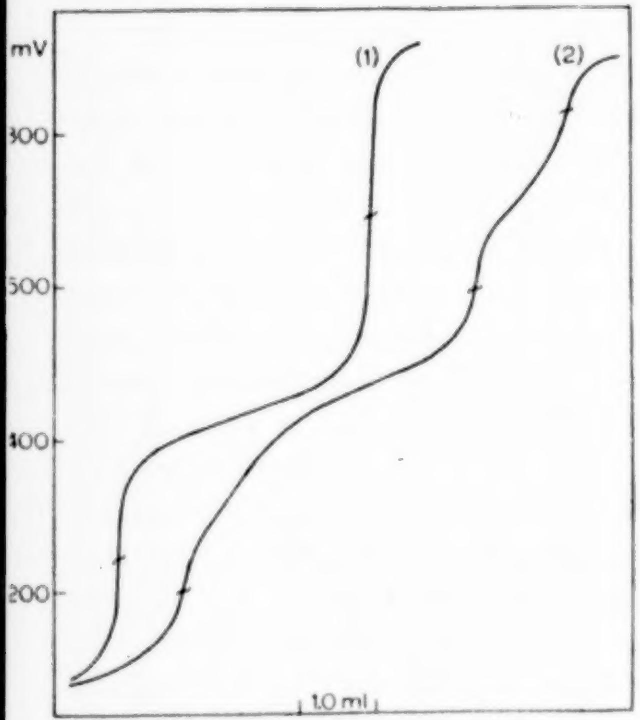

Fig. 2. Titration of uranium acetate, (1), and sodium phosphate, (2), after acidification with sulfuric acid.

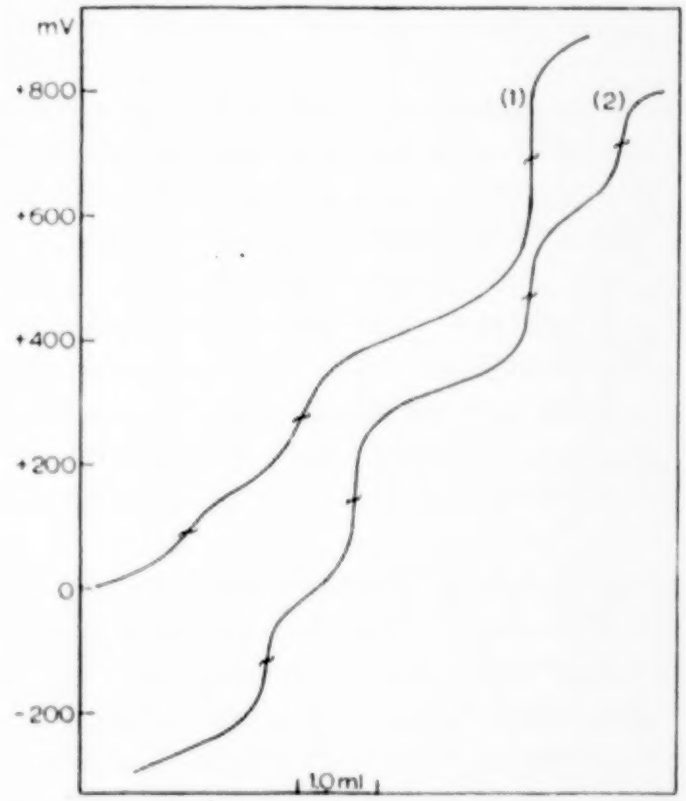

Fig. 3. Titration of sodium potassium tartrate, (1), and potassium hydrogen phthalate, (2), after acidification with sulfuric acid.

The titration of sodium phosphite, sulfuric acid, illustrated in Fig. 4, is of interest in that five inflections are discernible in the potentiometric curve. The first and fourth inflections represent neutralization of the two sulfuric acid equivalents, the volume of titrant from the first to the third end-point represents neutralization of the first phosphorous acid equivalent. The second end-point is equidistant from the first and third end-points and represents titration of one-half the phosphorous acid equivalent. The fifth inflection represents titration of the second phosphorous acid equivalent.

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Resolution of nitrate, nitrite mixtures

Nitrate, nitrite salt mixtures can be analyzed by this procedure. It was necessary in this analysis to hold the salt-acid reaction temperature below 5°. The titration of sodium nitrate and sodium nitrite mixtures after sulfuric acid acidification is illustrated in Fig. 5. The first inflection in the curve represents neutralization of the nitric acid and the first sulfuric acid equivalents, the second represents neutralization of the nitrous acid equivalent, and the third represents neutralization of the second sulfuric acid equivalent. The following calculations apply in determining the percent of each constituent in the mixture, titrating a 50-ml aliquot of the 100-ml dilution.

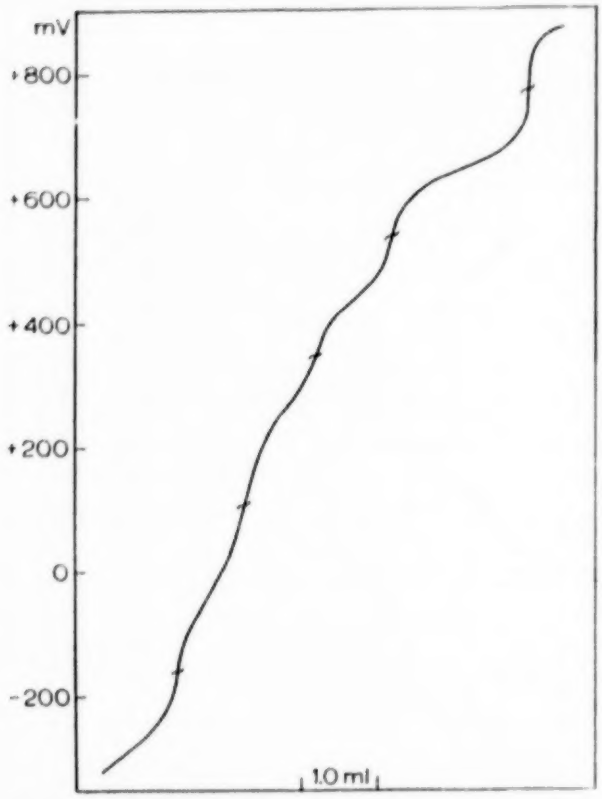

Fig. 4. Titration of sodium phosphite after acidification with sulfuric acid.

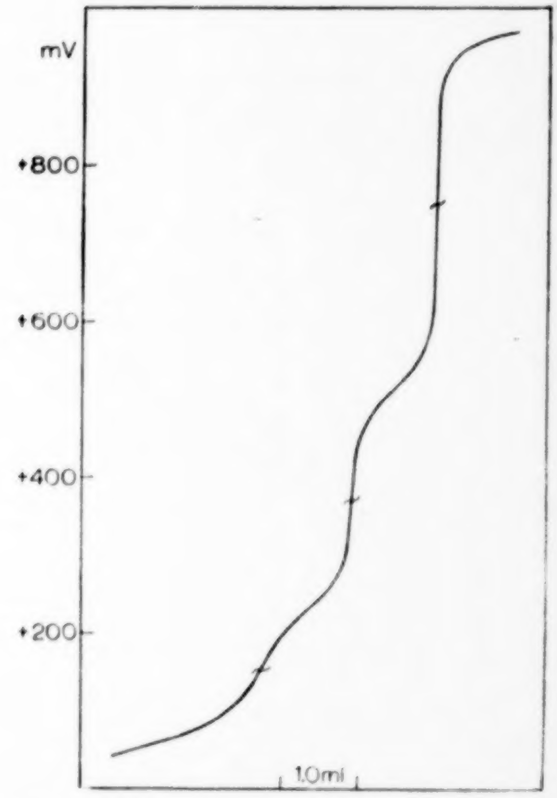

Fig. 5. Titration of sodium nitrite, sodium nitrate after acidification with sulfuric acid.

TABLE II

ANALYSIS OF SODIUM NITRATE—SODIUM NITRITE MIXTURES

Sodium nitrate			*Sodium nitrite*		
Added, mg	*Recovered, mg*	*% Recovery*	*Added, mg*	*Recovered, mg*	*% Recovery*
20.03	19.60	97.9	13.85	13.78	99.6
12.03	11.85	98.5	8.81	8.56	97.2
30.41	30.61	100.7	11.68	11.21	96.0
24.25	24.08	99.3	2.34	2.42	103.6
6.22	6.35	102.1	14.01	13.79	98.4

$$\%\ \text{Sodium nitrite} = \frac{2(V_2 - V_1)(N.F.)(6.901)}{\text{Sample wt.}}$$

$$\%\ \text{Sodium nitrate} = \frac{2[V_1 - (V_3 - V_2)](N.F.)(8.501)}{\text{Sample wt.}}$$

References p. 73

where V_1 = volume of titrant to first end-point.
V_2 = volume of titrant to second end-point.
V_3 = volume of titrant to third end-point.
$N.F.$ = normality of tetrabutylammonium hydroxide solution.

Results from the analysis of known mixtures of sodium nitrate and sodium nitrite are listed in Table II.

DISCUSSION

In the proposed procedure, it is essential that the salt undergo an anion-exchange reaction with the acidifying agent, and that the two acids be resolved by a differentiating titration. These requirements would be fulfilled by a very wide variety of salts.

The carbonate and hydroxide impurities, if present, do not interfere in this procedure. It is possible to ascertain the carbonate or hydroxide impurity in a salt by adding an exact volume of standard sulfuric acid when acidifying. Any carbonate present reacts to form carbon dioxide, water, and the sulfate salt, the hydroxide to form water and the sulfate salt, none of which are titratable under the specified conditions. In the ensuing titration, the volume difference between the final end-point, and that for a blank sulfuric acid determination is a measure of the carbonate or hydroxide impurity.

Analysis of salts of strong acids and weak bases are not included in this study as they may be titrated directly with tetrabutylammonium hydroxide. These salts are dissolved in a minimum amount of water, the nonaqueous solvent added and the solution then titrated. Salts in this category, if water-insoluble, but acid-soluble, may be dissolved in a minimum amount of acid, and a differentiating titration performed after addition of a nonaqueous solvent.

SUMMARY

The procedures suggested for the determination of salts in nonaqueous solutions have been limited almost wholly to the analysis of amine salts and salts of the alkali and alkaline earth metals. Other salts are usually assayed by a variety of specific cationic or anionic procedures. By the proposed method, salts of all types can be determined titrimetrically so long as the compound will participate in an anion-exchange reaction. The procedure simply involves acidification of the salt with an excess of a strong acid, addition of a nonaqueous solvent and a differentiating potentiometric titration. Carbonate and hydroxide impurities do not interfere in the analysis and the solubility difficulties experienced in other nonaqueous procedures are not encountered in this method.

RÉSUMÉ

Une méthode titrimétrique est proposée pour le dosage des sels minéraux, en milieu non aqueux. Le procédé consiste à traiter le sel à analyser par un acide fort; on ajoute ensuite un solvant non aqueux et on effectue le titrage par potentiométrie.

ZUSAMMENFASSUNG

Es wird eine Titrationsmethode zur Bestimmung von mineralsauren Salzen in nicht-wässrigen Lösungsmitteln beschrieben. Das Salz wird mit einem Überschuss einer starken Säure und dem nicht-wässrigen Lösungsmittel versetzt und anschliessend potentiometrisch titriert.

REFERENCES

[1] G. W. Kolling, *J. Chem. Educ.*, 34 (1957) 170.
[2] M. Schmall, C. W. Pifer and G. Wollish, *Anal. Chem.*, 24 (1952) 1446.
[3] R. H. Cundiff and P. C. Markunas, *Anal. Chim. Acta*, 20 (1959) 506.
[4] R. H. Cundiff and P. C. Markunas, *Anal. Chem.*, 28 (1956) 792.
[5] R. H. Cundiff and P. C. Markunas, *Anal. Chem.*, 30 (1958) 1450.

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DOSAGES EN ANALYSE MINÉRALE PAR EXTRACTION À L'AIDE DE CATIONS COLORÉS

III. DOSAGES PAR EXTRACTION À L'AIDE DE COLORANTS BASIQUES

A. DOSAGE DE TRACES D'OR PÀR LE VIOLET DE MÉTHYLE EN PRÉSENCE DE PLATINE

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Recherche du solvant

Les cations correspondants aux colorants basiques donnent avec certains anions des combinaisons extractibles par des solvants convenablement choisis. La recherche de la phase organique capable d'extraire aussi quantitativement que possible l'une de ces combinaisons est empirique car les connaissances actuelles sur les phénomènes de solvatation ne permettent pas de prévoir les solvants qui extraient une association donnée d'un anion et d'un cation. Toutefois l'expérience montre que seuls quelques solvants sont capables d'extraire les combinaisons d'un cation coloré donné. Précédemment, nous avons indiqué que les combinaisons de l'*o*-phénanthroline ferreuse étaient extractibles par le dichloro-1,2-éthane, l'alcool benzylique, l'*o*-nitrotoluène, l'*o*-bromotoluène. Le dichloro-1,2-éthane extrait quantitativement les combinaisons du bleu de méthylène avec les anions suivants: ClO_4^-, BF_4^-, IO_4^-, CNS^-, $Cl_3C{-}CO_2^-$, $AuCl_4^-$, $TlCl_4^-$. Les autres solvants chlorés: chloroforme, tétrachlorure de carbone, trichloréthylène; les hydrocarbures aromatiques et leurs dérivés halogénés, les cétones, esters, éthers, les plus courants ne dissolvent aucune de ces combinaisons.

On peut rechercher les solvants correspondant à un colorant donné, en utilisant l'une des combinaisons de ce colorant avec un anion en général facilement extractible comme CNS^- ou $Cl_3C{-}CO_2^-$. Il existe certainement des exceptions que cette méthode empirique ne permet pas de déceler, mais elle évite des essais fastidieux.

On trouvera quelques exemples dans le Tableau I:

TABLEAU I

Cations	*Solvants*
Violet de méthyle	trichloréthylène, toluène, *o*-bromotoluène, acétate de butyle, acétate d'isoamyle
Violet cristallisé	dipropylcétone (butyrone), méthylisobutylcétone (hexone)
Rouge neutre	cétones aromatiques, en particulier l'acétophénone
Safranine	acétophénone
Rhodamine B	benzène, acétate d'amyle, éther isopropylique

Les solvants utilisés doivent être très purs. En effet, la présence de traces d'acides organiques divers entraine souvent l'extraction du colorant en quantité telle, que tout dosage devient impossible. Les solvants chlorés en particulier doivent être redistillés, dans un appareil en verrerie rodée en l'absence de toute trace de corps gras. Cette purification est parfois insuffisante et doit être précédée d'un ou plusieurs lavages à l'aide de solutions alcalines.

Principe du dosage

Le complexe $AuCl_4^-$, comme ClO_4^-, IO_4^-, BF_4^-, $SbCl_4^-$, $TlCl_4^-$, $BiCl_4^-$, et plus généralement les anions du type LM_4^-, donne avec les cations de certains colorants basiques des combinaisons le plus souvent peu solubles dans l'eau, mais extractibles par une phase organique convenablement choisie. On a décrit par exemple, l'extraction du complexe $AuCl_4^-$ associé aux cations d'une benzylidène–rhodanine [1,2] (benzène, chloroforme) et de la rhodamine B[3] (éther isopropylique). Nous avons étudié l'extraction de ce complexe associé aux cations du bleu de méthylène (dichloro-1, 2-éthane) et du violet de méthyle (trichloréthylène). Ce dernier colorant a été finalement retenu pour la remarquable simplicité du mode opératoire. En effet, à un pH convenable, on peut extraire l'or et le séparer du platine dont le complexe $PtCl_6^{-2}$ n'est pas extractible. De même les ions Cl^- ne sont pas extraits; les nitrates gênent à partir d'une certaine concentration.

I. ÉTUDE DU DOSAGE DE L'OR

Réactifs utilisés

Solution de violet de méthyle. Solution aqueuse environ $10^{-3}M$ (0.4 g/l) du produit R.A.L. pour bactériologie.

Trichloréthylène. L'expérience montre qu'une simple distillation du produit ,,pur'' ou ,,technique'' est en général insuffisante pour éliminer certaines impuretés qui extraient d'importantes quantités de colorant. Le mode opératoire suivant a été adopté: après une première distillation, le solvant est placé dans une ampoule à décanter, et agité 2 fois pendant 5 min avec son demi-volume de soude normale, puis avec son volume d'eau distillée. Il est ensuite rectifié; on recueille la fraction passant à 87° ± 1°.

Solution d'or étalon. Une solution mère a été préparée par dissolution dans l'acide chlorhydrique normal d'environ 0.8 g de chlorure d'or par l. Le titre a été déterminé par gravimétrie (méthode à l'hydroquinone) et par volumétrie (iodométrie). La solution renfermait 0.360 g d'or par l. Elle a servi à préparer par dilution dans l'acide chlorhydrique $N/10$, une solution renfermant 5 μg d'or par ml.

Extraction de l'or

En désignant par HB^+ le cation coloré, la réaction d'extraction utilisée s'écrit:

$$\underset{\text{Eau}}{AuCl_4^- + HB^+} \rightleftharpoons \underset{\text{Trichloréthylène}}{(AuCl_4HB)_S}$$

A cet équilibre, correspond la relation

$$\frac{(AuCl_4^-)\ (HB^+)}{(AuCl_4HB)_S} = K$$

K étant fonction de la température.

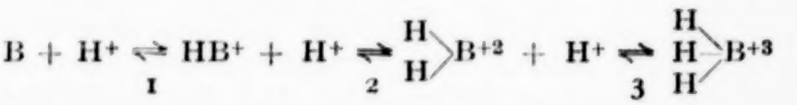
Le coefficient de partage apparent est fonction de K et de (HB^+)

$$\frac{(AuCl_4HB)_S}{(AuCl_4^-)} = \frac{(HB^+)}{K}$$

L'expérience montre que la précision optimum des dosages de traces à l'aide des colorants est de l'ordre de 1 à 2%; on peut donc considérer l'extraction comme quantitative lorsque le coefficient de partage apparent est supérieur à 100. Si la constante K est très faible, le coefficient de partage peut rester supérieur à cette valeur lorsque la température et (HB^+) qui représente en première approximation la concentration du cation coloré dans la phase aqueuse, varient entre certaines limites. Mais le plus souvent, la valeur de K est telle que l'extraction n'est plus quantitative. On peut cependant effectuer un dosage, à condition de maintenir constant le rapport $(HB^+)/K$, en contrôlant la température et en maintenant constante la concentration du cation coloré. Cette concentration est fonction: (a) essentiellement du pH, (b) à un pH donné, de la quantité de colorant extrait. Or cette méthode ne s'appliquant qu'au dosage des traces, la concentration de la combinaison extraite dans la phase organique est toujours très faible (10^{-6} à 10^{-5} par exemple). Il suffit donc de choisir une concentration initiale du colorant en phase aqueuse telle que la fraction extraite soit négligeable ou de l'ordre de grandeur des erreurs d'expériences.

Influence du pH

Nous avons désigné le cation coloré par HB^+. Or de nombreux colorants basiques possèdent plusieurs fonctions amines auxquelles correspondent des cations de couleurs différentes. C'est le cas du violet de méthyle, colorant pentaméthylé du groupe du triphénylméthane qui présente vraisemblablement deux fonctions amines tertiaires et une fonction amine secondaire. Les cations correspondants à ces bases très faibles n'existent qu'en milieu très acide. On peut schématiquement représenter les trois systèmes acide-base par les équilibres:



$$B + H^+ \underset{1}{\rightleftharpoons} HB^+ + H^+ \underset{2}{\rightleftharpoons} \begin{matrix}H\\H\end{matrix}\!>\!B^{+2} + H^+ \underset{3}{\rightleftharpoons} \begin{matrix}H\\H\\H\end{matrix}\!>\!B^{+3}$$

Des nombreuses expériences que nous avons effectuées avec des colorants de ce type, il résulte en accord avec les travaux de D. E. RYAN[4] que c'est le plus souvent le cation monochargé HB^+ qui est extrait. Or, les pK des systèmes précédents sont très voisins; le cation extractible HB^+ qui participe aux équilibres 1 et 2 n'existe donc que dans un domaine de pH très restreint.

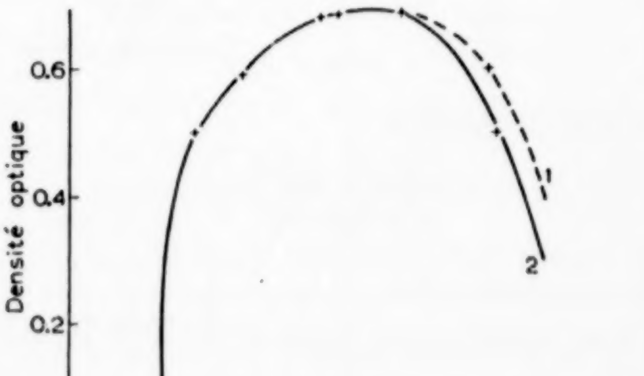


Fig. 1. Influence du pH sur l'extraction.

C'est dans ce domaine, correspondant à la concentration maximum du cation coloré HB^+, qu'il faut choisir le pH d'extraction afin d'obtenir le coefficient de partage apparent le plus élevé. Ceci n'est possible que si l'anion extractible existe à ce pH. Or, on sait que le complexe aurichlorhydrique $AuCl_4^-$ est très stable en milieu acide. Cependant en solution très diluée la stabilité de ce complexe peut-être fonction de la concentration des ions chlorures. Nous avons donc étudié l'extraction de cet anion en fonction du pH: (a) en maintenant constante la concentration des ions chlorures ($1 M$) par mélange de solutions d'acide chlorhydrique et de chlorure de potassium entre pH 0.2 et pH = 2 (courbe 1, Fig. 1), (b) à l'aide de solutions d'acide chlorhydrique de titres variés entre HCl 4N et pH = 2 (courbe 2, Fig. 1).

Les autres facteurs de l'extraction sont maintenus constants: quantité d'or (18 μg), concentration du colorant dans la phase aqueuse ($2 \cdot 10^{-4}$), volume de la phase aqueuse (15 ml), volume de trichloréthylène (15 ml), température (20°), temps d'agitation (3 min).

Les deux courbes confondues entre pH = 0.2 et pH = 1.1 restent ensuite voisines, ce qui confirme la stabilité du complexe en milieu acide. On voit d'autre part que l'extraction est maximum entre pH = 0.8 et pH = 1.1 ; elle est d'ailleurs quantitative ; une seconde extraction effectuée dans les mêmes conditions donne en effet une phase organique incolore.

Spectrophotométrie

L'appareil utilisé est le spectrophotomètre Jobin et Yvon, type „Maroc". Les spectres d'absorption de la molécule du colorant en milieu aqueux et de la combinaison extraite par le trichloréthylène sont représentés sur la Fig. 2.

La densité optique de la phase organique est mesurée au maximum d'absorption, soit pour $\lambda = 600.0$ mμ. La loi de Beer est suivie à ± 1% près (courbe 1 Fig. 3). Le coefficient d'extraction moléculaire à 20° est voisin de 115.000, ce qui permet de déceler avec une cuve de 2 cm une concentration limite de 10 à 15 μg d'or par l.

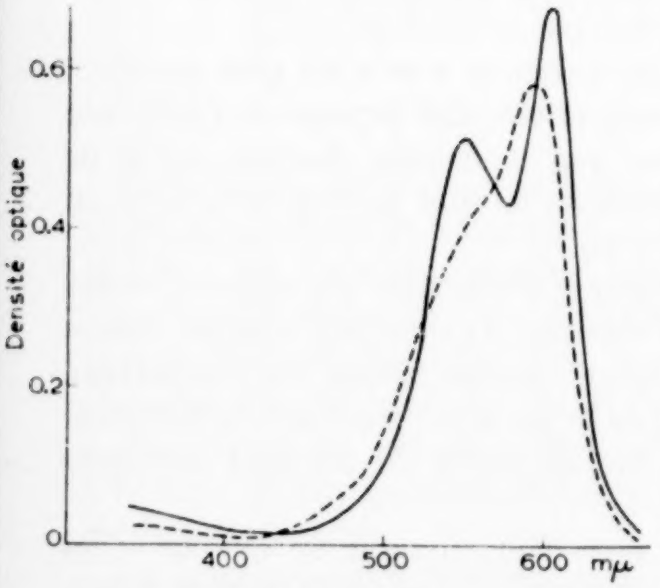


Fig. 2. Spectres d'absorption: - - -: de la molecule de „Violet de Méthyle" en solution aqueuse (4 mg/l) —— : du complexe dans le trichloréthylène.

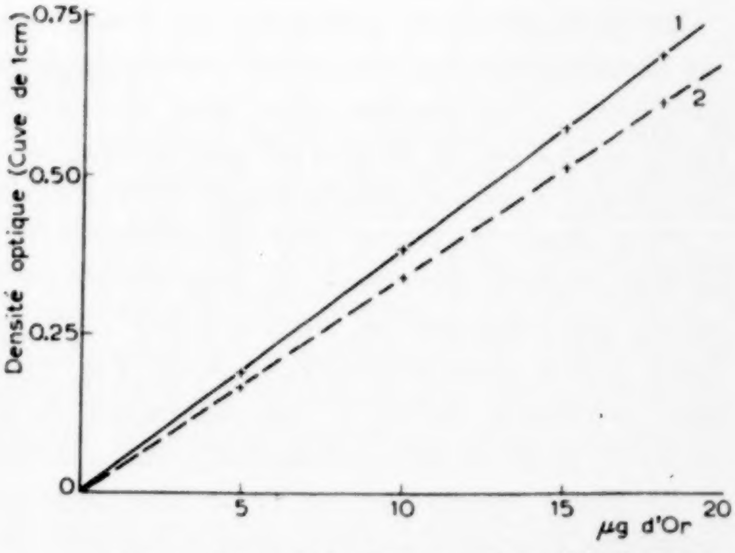


Fig. 3. Dosage de l'or: courbes d'étalonnage —— 1: à pH = 1 - - - - 2: en présence de platine à pH = 0.

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Cette méthode est plus sensible que celle décrite par MacNulty et Wollard[3] qui préconisent l'emploi de la rhodamine B. En effet, le coefficient d'extinction moléculaire calculé à partir des résultats publiés par ces auteurs est voisin de 72.000.

Mode opératoire pour le dosage des traces d'or

Il est facile de déduire des résultats précédents, un mode opératoire s'appliquant au dosage de l'or en l'absence d'autres éléments, en particulier d'autres métaux précieux. Par exemple, pour 10 ml d'une solution dont le pH est voisin de 1 : A 10 ml de la solution, ajouter 3 ml de la solution du colorant, 3 ml d'acide chlorhydrique 2 *N*/10, 15 ml de solvant. Agiter énergiquement trois minutes dans une ampoule à décanter non graissée. Après décantation, mesurer la densité optique de la phase organique à $\lambda = 600.0$ mμ. Un essai à blanc effectué dans les mêmes conditions en remplaçant la solution à doser par de l'acide chlorhydrique *N*/10, doit donner une phase organique incolore (la densité optique est généralement inférieure à 0.01). L'étalonnage est fait dans les mêmes conditions à l'aide d'une solution d'or de titre connu, renfermant par exemple 5 μg d'or par ml. Les nitrates gênent si leur concentration est supérieure à 10^{-4}.

II. DOSAGE DES TRACES D'OR EN PRÉSENCE DE PLATINE

Le complexe platichlorhydrique $PtCl_6^{-2}$ donne avec le cation monochargé du violet de méthyle un précipité:

$$PtCl_6(HB)_2 \underset{2}{\overset{1}{\rightleftharpoons}} PtCl_6^{-2} + 2\ HB^+$$

Ce composé peu soluble n'est pas extractible par le trichloréthylène et n'existe que dans le domaine de pH très restreint où se trouve le cation HB^+. Par exemple, avec une concentration du platine égale à $2 \cdot 10^{-3} M$ (0.4 g/l), et une concentration totale du colorant égale à $2 \cdot 10^{-4}$, le précipité n'existe qu'entre pH = 0.3 et pH = 2.3.

En présence de ce précipité, un dosage précis de traces d'or n'est plus possible: (a) la concentration du cation coloré devient très faible; elle dépend de l'équilibre précédent. L'extraction n'est plus quantitative, son rendement devient voisin de 60%. (b) La loi de Beer n'est plus suivie, les résultats ne sont pas reproductibles en particulier avec les quantités d'or inférieures à 10 μg.

Pour doser les traces d'or en présence de platine, il est donc nécessaire d'éviter la formation du précipité. Le plus simple est d'effectuer l'extraction à un pH convenable par exemple en milieu acide chlorhydrique normal. Dans ces conditions, l'extraction n'est plus quantitative (Fig. 1), mais le pH étant constant, la température contrôlée (20° ± 1° par exemple) et la concentration du colorant suffisante ($2 \cdot 10^{-4}$), la loi de Beer est suivie (courbe 2, Fig. 3).

Le mode opératoire est donc identique au précédent: il suffit de remplacer les solutions d'acide chlorhydrique *N*/10 par des solutions *N*. Les résultats sont reproductibles à 2% près environ.

En milieu acide chlorhydrique *N*, les nitrates ne gênent que si leur concentration est supérieure à $5 \cdot 10^{-2}$.

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RÉSUMÉ

Le complexe aurichlorhydrique $AuCl_4^-$, associé au cation du violet de méthyle, est extractible quantitativement vers $pH = 1$ par le trichloréthylène. Le coefficient d'extinction moléculaire est voisin de 115.000. A $pH = 1$, le complexe platichlorhydrique donne avec le colorant un composé peu soluble non extractible. En présence de ce précipité un dosage précis de l'or devient impossible; on peut éviter sa formation en effectuant le dosage vers $pH = 0$; la sensibilité diminue car l'extraction n'est plus quantitative.

SUMMARY

A description is given of the determination of traces of gold in solutions, either alone or in the presence of platinum, according to the extraction method, using methyl violet as complexing agent.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Spuren-Mengen Gold in reiner Lösung sowie neben Platin mit Hilfe von Methylviolett nach dem Extraktionsverfahren beschrieben.

BIBLIOGRAPHIE

[1] E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, 2nd Ed., Interscience Publishers, Inc., New York 1950, p. 349.
[2] N. S. POLUEKTOV, *Trudy Vsesoyuz. Konf. Anal. Khim.*, 2 (1943) 393.
[3] B. J. MACNULTY ET L. D. WOOLLARD, *Anal. Chim. Acta*, 13 (1955) 154.
[4] D. E. RYAN, *Analyst*, 79 (1954) 707.

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DOSAGES EN ANALYSE MINÉRALE PAR EXTRACTION À L'AIDE DE CATIONS COLORÉS

III. DOSAGES PAR EXTRACTION À L'AIDE DE COLORANTS BASIQUES

B. DOSAGE DE TRACES D'ÉTAIN PAR LE VIOLET CRISTALLISÉ

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PRINCIPE

Nous avons pensé que l'utilisation d'un colorant basique permettrait la mise au point d'une méthode aussi fidèle mais plus sensible que celles récemment proposées utilisant des réactifs nouveaux, comme par exemple les dérivés de la fluorone[1-3]. Nous avons recherché une combinaison extractible d'un complexe négativement chargé de Sn(II) ou Sn(IV) avec le cation d'un colorant basique. C'est finalement le complexe chlorhydrique de Sn(II) ($SnCl_4^{-2}$ ou $SnCl_3^-$) associé au violet cristallisé qui a été retenu. Le solvant utilisé est la 4-heptanone (butyrone ou dipropylcétone). L'hexone (méthylisobutylcétone) peut être également employée, mais la sensibilité du dosage diminue.

La principale difficulté rencontrée au cours de cette étude a été la réduction des traces d'étain stannique en étain stanneux. Une méthode simple utilisant les propriétés réductrices de Ti(III) en présence de cupferron a permis de résoudre ce problème.

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Réduction des traces d'étain stannique

En solution, l'étain se présente le plus souvent à l'état stannique. Pour que la méthode proposée soit utilisable, il est donc nécessaire de réduire les traces d'étain(IV) aussi rapidement et aussi quantitativement que possible, par une méthode compatible avec les exigences de l'extraction: température, pH, concentration des différents ions reproductibles dans les différents essais. Les méthodes classiques utilisant les métaux réducteurs à l'état pulvérulent comme le fer ou le zinc s'adaptent difficilement à la réduction des traces et ne respectent pas ces conditions: les résultats ne sont pas reproductibles. L'emploi de cations très réducteurs comme V^{+2} ou Cr^{+2} s'est révélé inefficace.

On sait que la réaction: $Sn(IV) + 2\ Ti(III) \rightarrow Sn(II) + 2\ Ti(IV)$ est lente et incomplète. Or, en présence de cupferron, elle devient rapide et pratiquement quantitative. On peut ainsi réaliser rapidement la réduction des traces d'étain stannique dans le récipient d'extraction en présence d'un excès de réducteur et obtenir des résultats reproductibles; les ions du titane ne gênent pas pour la suite du dosage.

ÉTUDE DES DIFFÉRENTS FACTEURS

Réactifs utilisés

Solution étalon d'étain. Une masse connue d'étain pur (1 g environ) est attaquée par le minimum d'acide chlorhydrique concentré; on complète ensuite à 500 ml avec de l'acide chlorhydrique normal. On prépare ensuite une solution renfermant 2 µg d'étain par ml, par dilution avec de l'acide chlorhydrique normal.

Solution de cupferron. A préparer au moment de l'utilisation: 1 g du produit „Prolabo R.P." dans 50 ml d'eau.

Solution de chlorure titaneux. 35 g de la solution commerciale à 15% „Prolabo" dans 150 ml d'acide chlorhydrique normal. Cette solution-mère est conservée en atmosphère d'azote. Pour le dosage, on prépare au moment de l'utilisation une solution diluée 5 fois par de l'acide chlorhydrique normal.

Solution de violet cristallisé. Solution aqueuse à 3 g/l du produit R.A.L. pour bactériologie. La solution est agitée 1/2 h puis filtrée sur creuset de verre fritté No. 2.

Solvant. La 4-heptanone (dipropylcétone, butyrone) pure du commerce est agitée dans une ampoule à décanter avec deux fois son demi-volume d'hydroxyde de sodium normal, puis avec son volume d'eau distillée. Elle est ensuite rectifiée dans un appareil en verrerie rodée, non graissée. On recueille la fraction distillant entre 141 et 144°.

Étude qualitative de l'extraction

L'expérience montre que l'extraction par la butyrone de la combinaison du complexe chlorhydrique de Sn(II) et du violet cristallisé est accompagnée de l'extraction du chlorhydrate de ce colorant. Les deux réactions sont:

$$\text{I}:\ \underset{\text{Eau}}{SnCl_4^{-2} + 2\ HB^+} \underset{2}{\overset{1}{\rightleftharpoons}} \underset{\text{Butyrone}}{(SnCl_4H_2B_2)_s}$$

$$\text{avec}\ \frac{(SnCl_4^{-2})\ (HB^+)^2}{(SnCl_4H_2B_2)_s} = K_1 \qquad (1)$$

$$\text{II}:\ \underset{\text{Eau}}{Cl^- + HB^+} \underset{2}{\overset{1}{\rightleftharpoons}} \underset{\text{Butyrone}}{(ClHB)_s}$$

$$\text{avec}\ \frac{(Cl^-)\ (HB^+)}{(ClHB)_s} = K_2 \qquad (2)$$

Le coefficient de partage apparent de l'extraction I peut s'écrire:

$$\frac{(SnCl_4H_2B_2)_s}{(SnCl_4^{-2})} = \frac{(HB^+)^2}{K_1} = \frac{K_2^2}{K_1}\ \ \frac{(ClHB)_s^2}{(Cl^-)^2}$$

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Pour que ce coefficient de partage soit constant, il est donc nécessaire: d'effectuer l'extraction à température constante (K et K' sont fonctions de la température), de maintenir constante la concentration des chlorures en phase aqueuse et celle du chlorhydrate en phase organique. La relation (2) montre que cette dernière condition sera réalisée si pour une concentration donnée des chlorures, (HB^+) qui représente en première approximation la concentration du cation coloré à l'équilibre est constant. Nous avons montré dans le mémoire précédent que la concentration du cation coloré est pratiquement constante, si l'extraction est effectuée à pH constant, en présence d'une concentration du colorant telle que la partie extraite est négligeable devant la quantité totale.

Le dosage des traces d'étain à l'aide du violet cristallisé est donc possible malgré l'extraction simultanée de chlorhydrate du colorant à condition que les facteurs suivants soient maintenus constants: température, pH, concentration des chlorures et du colorant en phase aqueuse.

On sait que le complexe $SnCl_4^{-2}$ n'est stable qu'en milieu acide chlorhydrique, à pH < 1. L'extraction de ce complexe s'effectue donc en présence d'une forte concentration d'ions Cl^-, et bien que le coefficient de partage de l'extraction II soit certainement très faible, la phase organique obtenue est fortement colorée, par la présence du chlorhydrate de violet cristallisé (la densité optique est voisine de 5). Un dosage spectrophotométrique direct est donc impossible. Pour éliminer la plus grande partie du chlorhydrate, il est nécessaire d'effectuer un lavage de la phase organique en l'agitant un certain temps avec un volume donné d'une solution aqueuse convenablement choisie. Cette opération a pour but de déplacer l'équilibre de la réaction II dans le sens 2, en limitant autant que possible le déplacement de celui de la réaction I dans le même sens. En particulier, la solution de lavage doit être choisie de telle manière que le complexe $SnCl_4^{-2}$ y soit stable, afin d'éviter des réactions qui déplaceraient l'équilibre, telles que:

$$\text{III: } SnCl_4^{-2} \rightleftharpoons SnCl_3^- + Cl^-$$

$$\text{IV: } SnCl_3^- + H_2O \rightleftharpoons SnOH^+ + H^+ + 3\,Cl^-$$

C'est dire que cette solution doit être une solution d'acide chlorhydrique ce qui est incompatible avec le déplacement total de l'équilibre II dans le sens 2. Afin de trouver les conditions optima nous avons étudié systématiquement le lavage de la phase organique par des solutions d'acide chlorhydrique de concentrations variées.

Lavage de la phase organique

Les résultats sont représentés par les courbes de la Fig. 1: la densité optique de la phase organique est portée en ordonnées, le titre en acide chlorhydrique de la phase aqueuse de lavage en abscisses.

La courbe 1 représente la densité optique de la butyrone, renfermant un mélange de chlorhydrate $(ClHB)_s$ et de la combinaison $(SnCl_4H_2B_2)_s$ après lavage par des solutions d'acide chlorhydrique de concentrations diverses.

La courbe 2 représente la densité optique de la butyrone ne renfermant que le chlorhydrate, après lavage par les mêmes solutions. Le volume de la phase aqueuse

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est le double de celui de la phase organique. Ces phases organiques sont obtenues par extraction dans des conditions opératoires décrites plus loin, la première d'une solution chlorhydrique renfermant une quantité connue d'étain (6 µg) la seconde d'une solution chlorhydrique identique ne renfermant pas d'étain; c'est ce que nous appelons „l'essai à blanc". La courbe 3 est la différence des courbes 1 et 2. Elle représente la densité optique de la combinaison ($SnCl_4H_2B_2$) seule; elle permet donc de déceler la concentration optimum de la solution chlorhydrique de lavage: 0.65*N*. C'est pour cette concentration que le déplacement de l'équilibre I dans le sens 2 est minimum, alors que le déplacement de l'équilibre II dans le sens 2 permet d'obtenir une densité optique de l'essai à blanc voisine de 0.30 (courbe 2), valeur suffisamment faible pour que des mesures spectrophotométriques précises soient possibles.

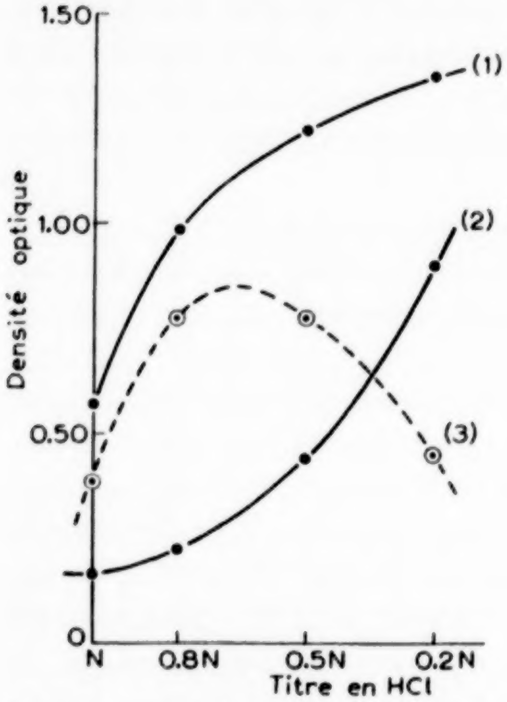

Fig. 1. Lavage de la phase organique.

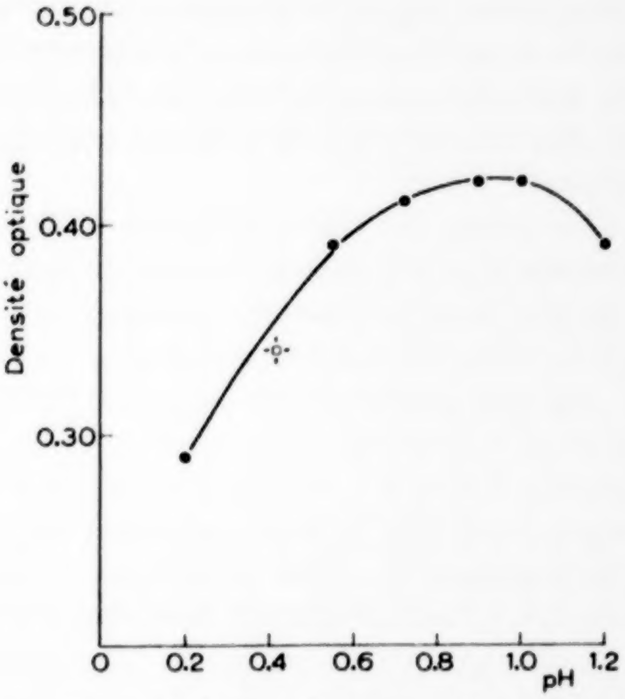

Fig. 2. Influence du pH sur l'extraction.

Influence et choix de la concentration du colorant

La concentration du colorant utilisée pour l'extraction influe doublement sur le résultat final. En effet le rendement de l'extraction dépend directement de cette concentration et nous avons montré qu'elle doit être suffisamment élevée pour que la quantité extraite soit négligeable devant la quantité totale. Mais ce qui précède montre d'autre part que la concentration du cation coloré HB^+ dans la phase aqueuse de lavage à l'équilibre dépend principalement du déplacement de l'équilibre II dans

TABLEAU I

Concentration du colorant au moment de l'extraction	*Densité optique de l'essai à blanc après lavage par HCl 0.65N*	*Densité optique de la phase organique après lavage par HCl 0.65N pour 6 µg d'étain*	*Différence*
$7.5 \cdot 10^{-4}$	0.19	0.95	0.76
$1.5 \cdot 10^{-3}$	0.32	1.17	0.85
$3 \cdot 10^{-3}$	0.51	1.46	0.95

le sens 2. Elle est donc fonction de la concentration initiale du chlorhydrate dans la phase organique et dépend finalement de la concentration du colorant au moment de l'extraction. Les résultats rassemblés dans le tableau ci-dessous montrent l'influence de cette concentration sur la valeur de l'essai à blanc et sur la sensibilité du dosage.

Nous avons adopté arbitrairement la concentration $1.5 \cdot 10^{-3}$ de manière à obtenir un essai à blanc de densité optique peu élevée (0.32).

Influence du pH

Les réactions III et IV montrent que la stabilité du complexe $SnCl_4^{-2}$ est fonction de la concentration des chlorures et du pH. Nous avons montré dans le mémoire précédent que la concentration du cation coloré HB^+ dépend également du pH. Pour étudier l'influence de ce facteur, il est donc nécessaire de maintenir constante la concentration des chlorures, en mélangeant par exemple des solutions de chlorure de potassium et d'acide chlorhydrique. En utilisant une concentration élevée de chlorure (1*M*) dans le but de stabiliser le complexe, l'expérience montre que le rendement de l'extraction passe par un maximum entre pH = 0.9 et pH = 1. La courbe obtenue est représentée sur la Fig. 2. La densité optique portée en ordonnées correspond à 3 μg d'étain extrait par 5 ml de solvant. On remarque que cette courbe est presque identique à celle qui figure dans le mémoire précédent, ce qui parait logique puisque les deux colorants utilisés sont très voisins. Mais, en présence d'une concentration moléculaire de chlorure, la densité optique de l'essai à blanc est trop élevée (0.70 à

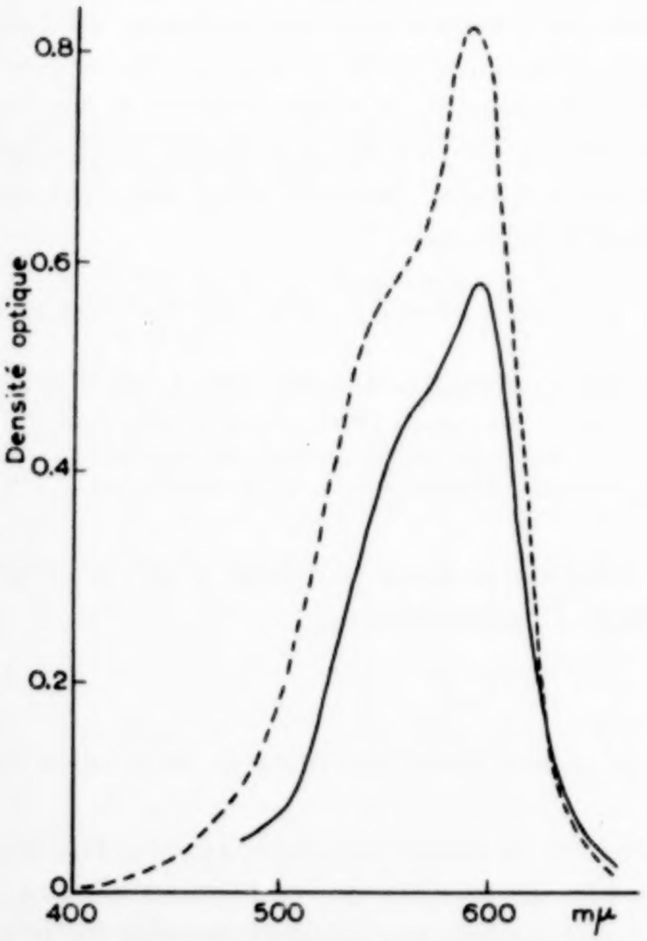

Fig. 3. Spectres d'absorption: . . . .: de la molécule de ,,Violet Cristallisé'' en solution aqueuse (4 mg/l); ——: du complexe dans la 4-heptanone.

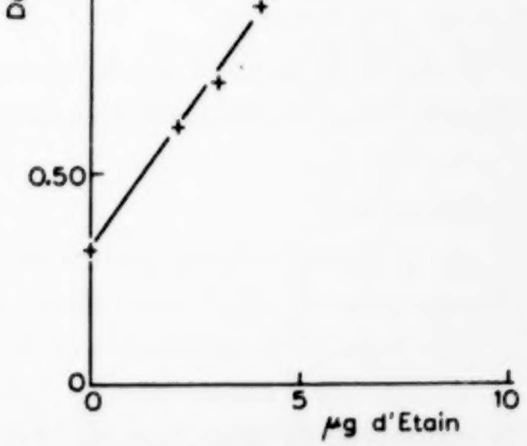

Fig. 4. Courbe d'étalonnage: pour le dosage de l'étain.

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pH = 0.9) pour que ces conditions soient utilisées pratiquement. Nous avons donc recherché la sensibilité optimum en fonction de la concentration de l'acide chlorhydrique seul. Le meilleur résultat est obtenu pour un titre égal à 0.3*N*, soit pour pH = 0.65 environ. La sensibilité obtenue dans ces conditions est voisine de celle des essais précédents effectués à pH = 0.9 en présence d'une concentration moléculaire des chlorures, mais la densité optique de l'essai à blanc est plus faible : 0.30 environ.

Spectrophotométrie

L'appareil utilisé est le spectrophotomètre Jobin et Yvon, type „Maroc". Les courbes de la Fig. 3 représentent les spectres d'absorption de la molécule de colorant en milieu aqueux et de la combinaison extraite par la butyrone. On voit que ces spectres sont très voisins et que le maximum d'absorption de la combinaison est situé à 595.0 mμ.

La loi de Beer est suivie, à ±2% près, même pour des valeurs de la densité optique de l'ordre de 1.50, comme le montre la courbe de la Fig. 4 obtenue avec une cuve d'une épaisseur de 1 cm. Ces résultats permettent de calculer un coefficient d'extinction moléculaire apparent : il est de 85.000 à 20°.

MODE OPÉRATOIRE

Pour 5 ml d'une solution d'étain dans l'acide chlorhydrique normal : dans une ampoule à décanter de 125 ml, non graissée, verser dans l'ordre : 5 ml de la solution à doser, 5 ml de soude 0.5*N*, 5 ml de solvant, 5 gouttes de la solution de cupferron (0.25 ml environ), 3 ml de la solution de colorant ; homogéniser puis ajouter 2 ml de la solution diluée de chlorure titaneux. Agiter énergiquement durant 5 min. exactement, puis laisser décanter. Dès que les deux phases sont séparées, éliminer la couche aqueuse inférieure. Verser ensuite dans l'ampoule 10 ml de la solution de lavage (acide chlorhydrique 0.65*N*), puis agiter durant 1 min. Aussitôt après décantation, effectuer la colorimétrie de la phase organique à 595.0 mμ.

Essai à blanc

Opérer de la même manière en remplaçant la solution à doser par 5 ml d'acide chlorhydrique normal.

Courbe d'étalonnage

Remplacer dans le mode opératoire la solution à doser par 5 ml d'une solution chlorhydrique normal renfermant une quantité connue d'étain.

Précautions

(a) le colorant étant lentement détruit en milieu acide à la lumière, la durée d'un dosage doit-être de l'ordre de 15 min.

(b) Un faible abaissement de la température de la phase organique après extraction et lavage (de l'ordre du 1/2 degré) provoque un trouble dû vraisemblablement à la formation de fines gouttelettes d'eau. Ce phénomène que nous avons observé avec d'autres solvants est réversible ; un léger réchauffement suffit pour obtenir une solution limpide.

Bibliographie p. 85

Influence de quelques ions

La présence des anions SO_4^{-2} et NO_3^- ne pertube pas le dosage; la sensibilité de la méthode ne varie pas; seule la densité optique de l'essai à blanc est modifiée. Par exemple pour une concentration des anions SO_4^{-2} ou NO_3^- égale à $5 \cdot 10^{-2}$, la densité optique de l'essai à blanc devient voisine de 0.50.

Certains cations qui présentent des complexes chlorhydriques comme: Sb(III), Tl(III), Bi(III), Cu(II) gênent car ils sont extractibles; d'autres comme Ge(IV), As(III), Pb(II), Co(II), Zn(II), Cr(III), ne modifient pas les résultats même si leur concentration est égale à 10^{-3}.

REMARQUES

(1) La butyrone peut-être remplacée par l'hexone, mais le rendement de l'extraction diminue: le coefficient d'extinction moléculaire apparent devient voisin de 30.000 à 20°.

(2) Le complexe oxalique de Sn(IV) associé au bleu de méthylène est extractible par le mélange acétophénone – 1,2-dichloréthane, mais une quantité importante d'oxalate de bleu de méthylène est extraite simultanément. Il est ensuite difficile de l'éliminer par lavage sans détruire la plus grande partie de la combinaison stannique.

RÉSUMÉ

Le complexe stannochlorhydrique $SnCl_4^{-2}$, associé au cation du violet cristallisé, est extractible vers pH = 1 par la 4-heptanone ou butyrone. L'extraction simultanée d'une petite quantité de chlorhydrate du colorant entraine un „lavage" de la phase organique par une solution d'acide chlorhydrique. Cette opération diminue la sensibilité, mais le coefficient d'extinction moléculaire apparent est encore très grand puisqu'il est voisin de 85.000.

SUMMARY

An extraction method is described for the determination of traces of tin in which crystal violet is used as complexing agent.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Spuren-Mengen von Zinn mit Hilfe von Kristallviolett nach dem Extraktionsverfahren.

BIBLIOGRAPHIE

[1] V. A. NAZARENKO ET N. V. LEBEDEVA, *Zhur. Anal. Khim.*, 10 (1955) 289.
[2] C. L. LUKE, *Anal. Chem.*, 28 (1956) 1276.
[3] L. B. GINZBURG ET E. P. SHKROBOT, *Zavodskaya Lab.*, 23 (1957) 527.

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DOSAGES EN ANALYSE MINÉRALE PAR EXTRACTION À L'AIDE DE CATIONS COLORÉS

III. DOSAGES PAR EXTRACTION À L'AIDE DE COLORANTS BASIQUES

C. DOSAGE DE TRACES DE PHOSPHATE PAR LA SAFRANINE

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BUT ET PRINCIPE

Pour certaines recherches dans le domaine des semi-conducteurs, la sensibilité des méthodes classiques de dosage de traces de phosphate est insuffisante (complexe phospho-vanado molybdique, réduction du complexe phosphomolybdique). Nous avons pensé que l'utilisation d'un colorant basique permettrait d'améliorer la sensibilité, et d'atteindre celle des méthodes radiochimiques lorsqu'elles sont appliquées au cas défavorable du silicium, en présentant l'avantage d'une plus grand rapidité d'exécution.

Les anions phosphates ne semblent pas donner avec les colorants basiques des combinaisons extractibles. Les phosphomolybdates et les phosphotungstates donnent avec des colorants basiques des groupes des azines, des thiazines et du triphénylméthane, des combinaisons peu solubles dans l'eau et dans les liquides organiques les plus courants. Cependant certains colorants comme le rouge neutre et la safranine associés à ces anions donnent à un pH convenable une combinaison extractible par quelques cétones aromatiques en particulier par l'acétophénone. Ce liquide possède une viscosité assez élevée et une densité voisine de celle de l'eau qui rend difficile la séparation des phases. On peut modifier ces propriétés par addition d'un solvant chloré peu volatil comme l'*o*-dichlorobenzène sans modifier profondément les phénomènes de solvatation.

Le molybdate ajouté en excès pour former l'anion phosphomolybdique précipite presque totalement le colorant. Mais l'expérience montre que le précipité très peu soluble dans la phase organique, se rassemble lors de l'extraction à l'interface et ne gêne pas dans certaines conditions la reproductibilité des résultats. Toutefois la loi de Beer n'est pas suivie; il est donc nécessaire d'établir une courbe d'étalonnage.

ÉTUDE DES DIFFÉRENTS FACTEURS DU DOSAGE

Réactifs utilisés

Acide sulfurique pour toxicologie. Solvant. C'est un mélange renfermant trois volumes d'acétophénone pour un volume d'*o*-dichlorobenzène. Ces deux liquides sont préalablement rectifiés sous vide dans un appareil en verrerie rodée, non graissée.

Solution de molybdate. Solution aqueuse $10^{-3}M$ de molybdate d'ammonium R.P. [$(NH_4)_6Mo_7O_{24}$, 4 H_2O], soit 1.25 g/l.

Solution de safranine. Solution aqueuse à 2 g/l du produit R.A.L. pour microbiologie. La solution agitée pendant 30 min est ensuite filtrée sur un creuset de verre fritté No. 2.

Solution étalon de phosphate. On prépare une solution-mère renfermant 300 μg de phosphore par ml, à l'aide de phosphate disodique R.P. (Na_2HPO_4, 12 H_2O), soit 3.47 g/l. Par dilution avec de l'eau distillée, on obtient une solution étalon renfermant 0.6 μg de phosphore par ml.

Influence du pH

Plusieurs facteurs dépendent du pH:
- la solubilité du précipité de molybdate de safranine,
- l'existence du cation coloré HB^+. Nous avons montré dans les mémoires précédents qu'il n'existe qu'en milieu acide.
- la stabilité du complexe phosphomolybdique.

La variation du pH est obtenue par addition d'acide sulfurique; les autres facteurs sont maintenus constants: phosphate ajouté (2 ml de la solution étalon, soit 1.2 µg de phosphore), volume de la solution de molybdate (4 ml) et de la solution de safranine (1 ml), volume total de la phase aqueuse (20 ml) et de la phase organique (10 ml), température (20°), temps d'agitation (5 min).

Les résultats sont représentés par la courbe de la Fig. 1; la densité optique portée en ordonnées représente la différence entre la densité optique de l'essai renfermant 1.2 µg de phosphore ajouté et celle de ,,l'essai à blanc'' effectué dans les mêmes conditions (les 2 ml de la solution étalon sont remplacés par de l'eau distillée). La cuve a 1 cm d'épaisseur, on voit que le maximum de sensibilité est atteint dans un domaine de pH restreint, entre pH = 1.4 et pH = 1.6.

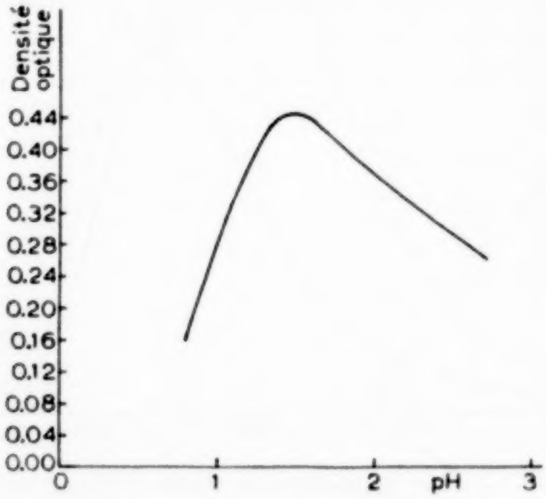

Fig. 1. Influence du pH sur l'extraction du phosphomolybdate de safranine (1,2 µg de phosphore).

Spectrophotométrie

L'appareil utilisé est le spectrophotomètre Jobin et Yvon, type ,,Algérie''.

L'essai à blanc présente une densité optique assez élevée, de l'ordre de 1,5 unités; cette coloration provient des traces de phosphate que renferment les réactifs et d'une légère solubilité du précipité de molybdate de safranine. Cette valeur est trop grande pour permettre une spectrophotométrie directe, mais suffisamment faible pour qu'une spectrophotométrie différentielle soit possible. L'essai à blanc est donc utilisé pour le règlage du zéro de l'appareil de mesures (densité optique = 0; transmission = 100).

L'expérience montre d'autre part que les résultats ne sont reproductibles (à 0.02 unité de densité optique près) que si l'on abandonne le précipité de molybdate de safranine pendant au moins 10 min avant l'extraction.

Le spectre d'absorption du phosphomolybdate de safranine dans le solvant et celui de la molécule du colorant dans l'eau sont représentés sur la Fig. 2. La densité optique de la phase organique est mesurée au maximum d'absorption, soit pour $\lambda = 532.5$ mμ.

La loi de Beer n'est pas suivie : la courbe d'étalonnage de la Fig. 3 montre que la sensibilité augmente avec la quantité de phosphate extrait.

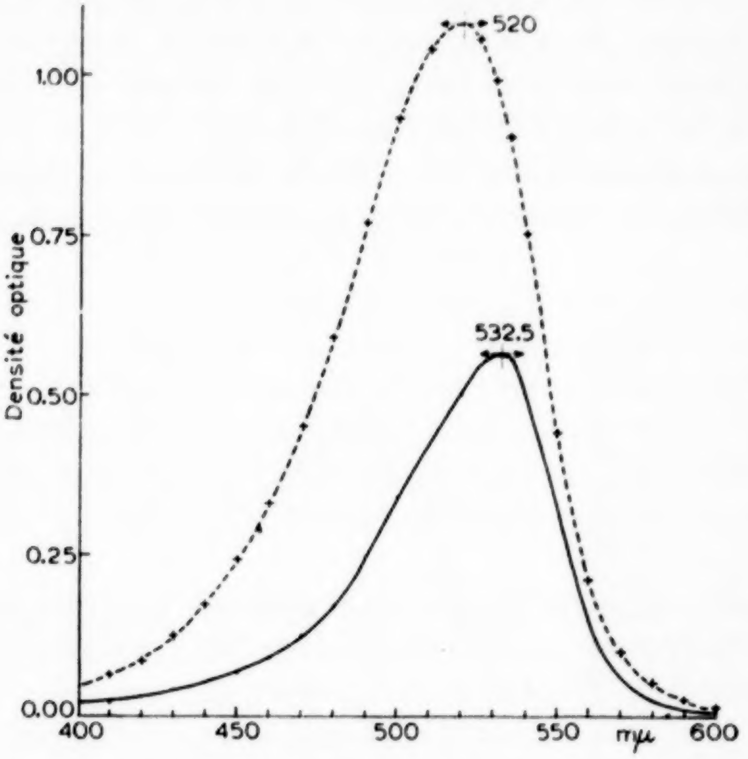

Fig. 2. Spectres d'absorption: .... de la safranine dans l'eau; —— du phosphomolybdate de safranine dans le solvant.

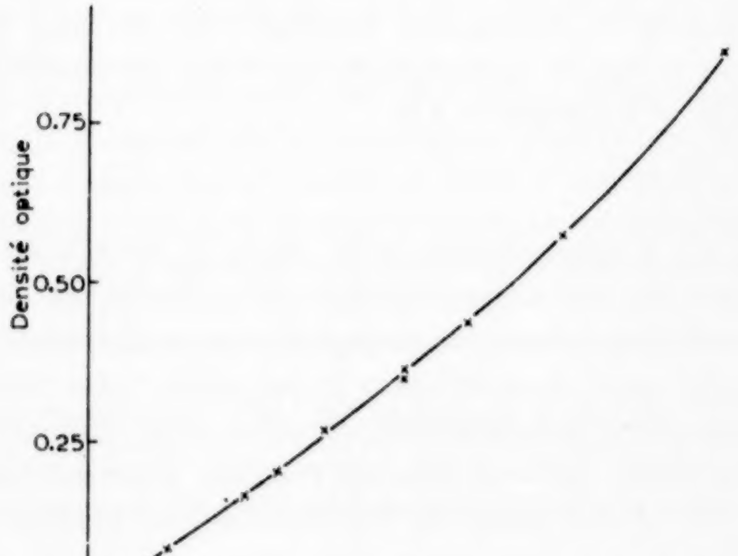

Fig. 3. Courbe d'étalonnage pour le dosage du phosphore.

La réaction d'extraction est pratiquement quantitative comme le prouve l'expérience suivante : on compare la densité optique d'un essai renfermant 1.2 µg de phosphore à celle de l'essai à blanc. D'après la courbe d'étalonnage de la Fig. 3, la différence est voisine de 0.44. Les deux phases aqueuses renfermant le précipité sont recueillies et une seconde extraction est effectuée dans les mêmes conditions. Les deux phases organiques obtenues présentent alors la même densité optique, qui en valeur absolue est inférieure d'environ 40% à celle de l'essai à blanc initial. Ceci prouve d'une part qu'une seule opération suffit pour que la réaction d'extraction soit quantitative d'autre part que la coloration obtenue après la seconde opération provient d'une légère solubilité du précipité de molybdate de safranine.

Bien que la loi de Beer ne soit pas suivie, on peut calculer un coefficient d'extinction moléculaire moyen pour une quantité donnée de phosphore extrait. D'après la courbe d'étalonnage, on obtient par exemple 116.000 entre 0 et 1 µg et 155.000 entre 1 et 2 µg. Il est d'ailleurs possible d'utiliser cette dernière sensibilité; il suffit, d'ajouter 1 µg de phosphore à l'essai à blanc et à la solution à doser. La Fig. 4 présente une courbe d'étalonnage obtenue dans ces conditions: on voit que la courbe devient pratiquement rectiligne lorsque la quantité de phosphore extrait augmente; le coefficient d'extinction moléculaire correspondant à cette partie de la courbe est voisin de 190.000.

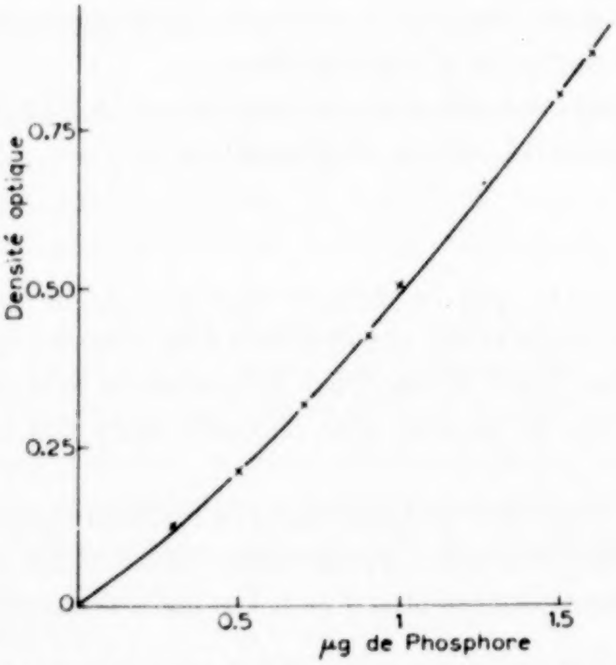

Fig. 4. Courbe d'étalonnage après addition de 1 µg de phosphore.

Concentration du molybdate et du colorant

Les volumes des solutions de molybdate et de safranine sont choisis de manière qu'il reste dans la phase aqueuse après la formation du précipité un large excès de molybdate pour la formation du complexe phosphomolybdique.

Au pH optimum (1.5), le précipité n'est que légèrement soluble, la concentration du cation coloré est donc très faible. Malgré ces conditions apparemment défavorables, l'expérience montre que l'extraction est quantitative.

Influence de quelques ions

Le dosage peut-être effectué en présence de chlorures. Par contre les anions minéraux suivants sont extraits: arséniate, arsénite, vanadate, perchlorate, nitrate ainsi que certains anions organiques: thiocyanate, trichloracétate.

En milieu chlorhydrique, les cations donnant des complexes du type ACl_4^- gênent car ils sont extraits: Au(III), Bi(III), Tl(III), Sb(III).

MODE OPÉRATOIRE

Nous avons adopté le mode opératoire suivant:

Placer dans une ampoule à décantation de 125 ml non graissée 5 ml de la solution neutre de phosphate à doser, 10 ml d'acide sulfurique $N/10$, 4 ml de la solution de molybdate, 1 ml de la solution de safranine. Homogénéiser, abandonner durant 10 min. Ajouter ensuite 10 ml de solvant; agiter énergiquement durant 5 min. Après décantation (15 min. environ), recueillir la majeure partie de la phase organique et la centrifuger. Effectuer immédiatement la spectrocolorimétrie différentielle à 532.5 mμ en cuve de 1 cm, en réglant le zéro de l'appareil de mesures à l'aide d'un essai à blanc effectué *parallèlement* dans des conditions identiques en remplaçant la solution de phosphate à doser par 5 ml d'eau distillée.

La courbe d'étalonnage est obtenue en remplaçant la solution à doser par une solution renfermant une quantité connue de phosphore.

Précautions

(a) L'expérience montre que la densité optique de la phase organique diminue lentement avec le temps (environ 2/100 d'unité de densité optique par heure). Il est donc recommandé d'une part, d'effectuer en parallèle le dosage et l'essai à blanc et d'autre part, d'effectuer la mesure des densités optiques immédiatement après la centrifugation.

(b) Comme nous l'avons déjà indiqué dans le mémoire précédent, un léger abaissement de la température provoque l'apparition d'un trouble dans la phase organique, dû à la formation de fines gouttelettes d'eau. Un léger réchauffement rend à la solution sa limpidité.

RÉSUMÉ

Les anions phosphates ne semblent pas donner avec les colorants basiques des combinaisons extractibles. Par contre, les phosphomolybdates associés à certains colorants sont extractibles par des cétones aromatiques. Avec la safranine l'extraction par l'acétophénone est quantitative à pH = 1.5. Il est nécessaire d'établir une courbe d'étalonnage, la loi de Beer n'étant pas suivie. La sensibilité est très grande; une partie de la courbe d'étalonnage présente un coefficient d'extinction moléculaire moyen voisin de 190.000.

SUMMARY

An extraction method is described for the determination of traces of phosphate in the form of phosphomolybdate, in which safranine is used as complexing agent.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Spuren-Mengen von Phosphat in Form von Phosphormolybdat mit Hilfe von Safranin nach dem Extraktionsverfahren.

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DOSAGES EN ANALYSE MINÉRALE PAR EXTRACTION À L'AIDE DE CATIONS COLORÉS

III. DOSAGES PAR EXTRACTION À L'AIDE DE COLORANTS BASIQUES

D. DOSAGE DE TRACES DE SULFATE PAR LE BLEU DE MÉTHYLÈNE

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PRINCIPE

Nous avons essayé d'appliquer au dosage de traces de sulfate la méthode développée dans les mémoires précédents : associer à l'anion à doser le cation d'un colorant basique pour former une combinaison extractible par un solvant convenablement choisi. De nombreux colorants des groupes des azines, thiazines, triphénylméthane ont été essayés sans succès. La propriété que présente l'ion sulfate de donner des composés peu solubles dans l'eau avec certaines diamines ou polyamines primaires de masse moléculaire élevée, comme la benzidine et ses dérivés, se retrouve avec les colorants basiques : la thionine ou violet de Lauth, le brun Bismarck par exemple précipitent quantitativement avec les ions sulfates, mais nous n'avons pas trouvé le solvant approprié.

Nous avons alors pensé qu'il était possible de développer une méthode générale permettant de substituer aux anions à doser non extractibles comme les ions sulfates, des anions facilement extractibles en utilisant une résine anionique. Nous avons choisi l'ion thiocyanate qui présente moins d'affinité pour les résines que l'ion sulfate, et qui associé aux cations de nombreux colorants basiques donne des combinaisons facilement extractibles. Par exemple, avec le bleu de méthylène la combinaison est soluble dans le dichloro-1,2-éthane.

La réaction utilisée s'écrit:

$$\underset{\text{résine}}{2\,\mathrm{CNS}^-} + \underset{\text{solution}}{\mathrm{SO_4}^{-2}} \rightleftharpoons \underset{\text{résine}}{\mathrm{SO_4}^{-2}} + \underset{\text{solution}}{2\,\mathrm{CNS}^-}$$

DOSAGE DES IONS THIOCYANATES PAR LE BLEU DE MÉTHYLÈNE

L'anion CNS^- associé au bleu de méthylène est extractible quantitativement en milieu acide (vers $\mathrm{pH} = 1$) par le dichloro-1,2-éthane. Nous avons adopté le mode opératoire suivant:

Réactifs utilisés

Ils sont préparés avec de l'eau bidistillée dans un appareil en quartz.

Acide sulfurique 2N/10.

Solution de colorant. Solution aqueuse à 3 g/l du produit R.A.L. médicinal; la solution agitée pendant 30 min est ensuite filtrée sur creuset de verre fritté No. 2.

Dichloro-1,2-éthane. Le produit commercial pur est lavé deux fois dans une ampoule à décanter pendant quelques minutes par son demi-volume de soude normale, puis par son volume d'eau distillée. Il est ensuite distillé dans un appareil en verrerie rodée non graissée; on recueille la fraction distillant à 83° ± 1°.

Mode opératoire

Dans une ampoule à décanter de 125 ml non graissée, placer 10 ml de solvant, 5 m d'acide sulfurique $2N/10$, 1 ml de solution du colorant et 5 ml de la solution à doser. Agiter énergiquement pendant 3 min. Laisser décanter, puis séparer la couche organique et la centrifuger. Mesurer la densité optique pour $\lambda = 660.0$ mμ.

,,L'essai à blanc'' est effectué dans les mêmes conditions en remplaçant la solution à doser par de l'eau bidistillée. Il présente une densité optique voisine de 0.50 qui est due à une légère solubilité du sulfate de bleu de méthylène.

La Fig. 1 représente la droite d'étalonnage obtenue en remplaçant dans le mode opératoire la solution à doser par une solution de thiocyanate de potassium (R. P Prolabo) de titre connu. Les densités optiques (cuve de 1 cm) figurent en ordonnées et les concentrations des solutions de thiocyanate de potassium utilisées en abscisses. L'appareil utilisé est le spectrophotomètre Jobin et Yvon type ,,Algérie''. Le coefficient d'extinction moléculaire est voisin de 74.000.

Préparation de la résine. Essai à blanc

Nous avons utilisé la résine Dowex-1 X 4, 200 – 400 mesh commercialement sous forme de chlorure. Elle est traitée de la façon suivante : 30 g de résine humide sont agités dans un flacon pendant 20 min. avec deux fois 50 ml de solution $N/10$ de thiocyanate de potassium R. P., puis trois fois avec 50 ml de solution $2N$. La résine est filtrée et lavée à l'eau distillée entre chaque agitation. Elle est ensuite agitée de la même façon quatre fois avec 100 ml d'eau distillée, filtrée et abandonnée durant 48 heures dans l'eau distillée.

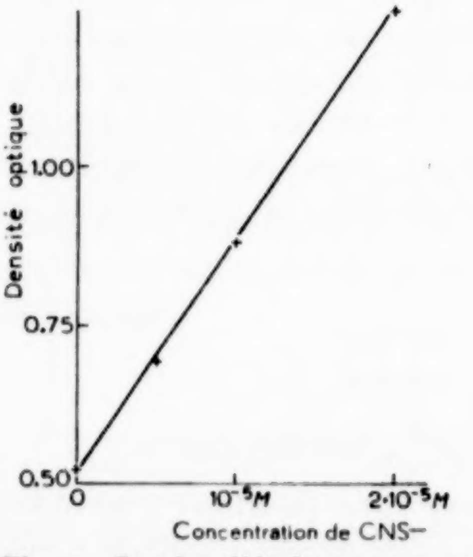

Fig. 1. Courbe d'étalonnage pour le dosage du thiocyanate.

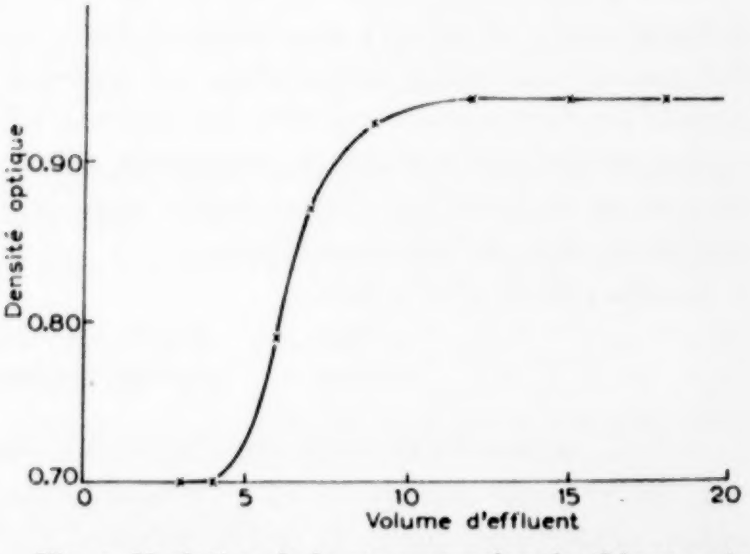

Fig. 2. Variation de la concentration du thiocyanate dans l'effluent en fonction du volume écoulé.

La résine est ensuite placée dans une colonne d'un diamètre de 1 cm, sur une hauteur de 15 cm. On fait ensuite passer sur la colonne de l'eau bidistillée (dans un appareil en quartz) par portion de 25 ml. La compacité du remplissage de la colonne est telle que le robinet étant ouvert au maximum, le débit est suffisamment lent : 25 ml en 15 min. On recueille les 5 derniers ml de chaque portion et l'on dose les ions thiocyanates par la méthode indiquée ci-dessus. Le lavage est poursuivi tant que la densité optique de ce dosage décroit. Elle doit ensuite rester constante à 0.01 unité près, si l'on observe les précautions relatives aux variations de température indiquées ci-dessous.

Nous avons trouvé la densité optique de l'essai à blanc à 21° égale à 0.81 ± 0.01.

Étalonnage. Dosage des traces de sulfate

Une solution de sulfate de potassium exactement $10^{-2} M$ est préparée par pesée du sel Prolabo R. P. Par dilution on obtient une gamme de solutions dont les titres s'échelonnent entre 10^{-6} et $2 \cdot 10^{-5} M$.

On trace ensuite la courbe représentant les variations de la concentration des ions thiocyanates dans l'effluent en fonction du volume, lorsqu'une solution de sulfate traverse la colonne. La courbe de la Fig. 2 a été obtenue de la manière suivante: on fait affleurer le niveau de l'eau distillée restant dans la colonne juste à la partie supérieure de la résine; on introduit ensuite dans la colonne avec précautions 25 ml d'une solution $10^{-5} M$ de sulfate. On recueille l'effluent par portions de 3 ml, et l'on effectue le dosage des ions thiocyanates. Afin de ne pas modifier le mode opératoire décrit ci-dessus on ajoute 2 ml d'eau bidistillée aux 3 ml d'effluent. Les densités optiques sont portées en ordonnées, le volume d'effluent en abscisses. Les premières portions recueillies présentent une densité optique de 0.70, valeur de l'essai à blanc pour 3 ml de solution. Le volume d'effluent correspondant à cette valeur (4 ml environ) représente la somme du volume interstitiel et du volume mort à la partie inférieure de la colonne. Cette courbe permet de déterminer à partir de quel volume la concentration des ions thiocyanates est constante. On peut donc éliminer la première partie de l'effluent, et ne conserver pour le dosage que le volume correspondant à la concentration maximum.

Nous avons finalement adopté le mode opératoire suivant valable pour l'étalonnage et le dosage d'une solution inconnue:

Faire affleurer le niveau de la solution restant dans la colonne juste à la partie supérieure de la résine. Introduire avec précautions 25 ml de la solution à doser (ou de la solution de titre connu). Recueillir les quinze premiers ml, les rejeter,

TABLEAU I

Concentration des solutions de sulfate	*Temp. = 21°*	*Densité optique colorimétrie différentielle cuve de 1 cm*
0		0
$10^{-6} M$		0.045
		0.052
$2 \cdot 10^{-6} M$		0.105
		0.117
$5 \cdot 10^{-6} M$		0.250
		0.255
$10^{-5} M$		0.495
		0.510
$2 \cdot 10^{-5} M$		0.97
		0.98

recueillir ensuite les dix derniers ml dans un récipient propre et sec. Prélever 5 ml et doser les ions thiocyanates comme il est indiqué ci-dessus.

La densité optique de l'essai à blanc étant élevée (0.80 environ) il est préférable d'effectuer une colorimétrie différentielle pour $\lambda = 660.0$ mμ en règlant le zéro de l'appareil à l'aide de cet essai (transmission = 100, densité optique = 0).

Les résultats sont rassemblés dans le Tableau I.

Influence de la température.

La reproductibilité des résultats dépend essentiellement de la température. Il est indispensable que les solutions utilisées soient amenées à la température du laboratoire. Celle-ci doit-être constante à 0.5° près. Il faut soustraire la colonne à tout rayonnement thermique: rayons solaires étuve, ampoule électrique, etc. On peut l'isoler à l'aide d'un enroulement de toile d'amiante par exemple.

RÉSUMÉ

Les ions sulfates ne semblent pas donner avec les colorants basiques des combinaisons extractibles. Une méthode générale, utilisant une résine anionique permet de substituer aux anions à doser non extractibles comme les sulfates, des ions facilement extractibles comme les thiocyanates: la solution diluée de sulfate passe sur une colonne de résine Dowex-1 X 4 préalablement mise sous forme thiocyanate. Les ions thiocyanates libérés, associés aux cations du bleu de méthylène sont extractibles quantitativement à pH = 1 par le dichloro-1,2-éthane. La méthode permet de doser des concentrations très faibles de sulfate ($10^{-6}M$).

SUMMARY

A method is described for the determination of traces of sulphate. By means of an exchange resin the sulphate ions are exchanged with an equivalent amount of thiocyanate ions and these are determined by the extraction method using methylene blue as complexing agent.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Spuren-Mengen Sulfat beschrieben. Das Sulfat-Ion wird mit Hilfe eines Austauscher-Harzes gegen eine äquivalente Menge Thiocyanat-Ion ausgetauscht und dieses mit Methylenblau nach dem Extraktionsverfahren bestimmt.

Reçu le 15 octobre 1958

Short Communications

Detection of the heavier rare-earth metal ions with several organic reagents

In previous studies, the detection of the lighter trivalent rare-earth ions with oxalic acid, cupferron, 8-quinolinol, and 2-methyl-8-quinolinol was reported[1,2]. Since only the rare-earth ions from lanthanum to gadolinium were studied, this investigation reports the detection of the heavier rare-earth ions with the same reagents.

The procedure for the sensitivity tests was essentially a modification of the method of IRVING, BUTLER, AND RING.[3] Tests were conducted in 15 by 145 mm test tubes

containing a known amount of 0.01 *M* or 0.001 *M* rare-earth metal chloride solution. For the oxalic acid and cupferron tests, 0.2 ml of 0.1 *M* reagent was added to the rare-earth solutions, diluted with water to 7.0 ml, and then heated for 10 min at 70°. The solutions were allowed to cool to room temperature and observed visually for the presence of a precipitate. A similar procedure was followed for the 8-quinolinol and 2-methyl-8-quinolinol tests except that 0.2 ml of the 0.1 *M* reagent in 95% ethanol was added to the rare-earth solutions containing 2.0 ml of an NH_4Cl–NH_4OH buffer, and then diluted with water to a total volume of 7.0 ml. The pH of the resulting solution was 9.5.

TABLE I

RESULTS OF SENSITIVITY TESTS

Metal ion	$\mu g\ M^{+3}$ *per ml*			
	Oxalic acid	*Cupferron*	*8-Quinolinol*	*2-Methyl 8-quinolinol*
Europium	35	5.2	1.7	17
Terbium	36	7.1	1.4	7.1
Dysprosium	19	7.4	1.1	7.4
Holmium	38	13	3.8	13
Erbium	57	17	3.8	9.5
Ytterbium	40	30	4.0	20

The results of the sensitivity tests are given on Table I. By far the best reagent for the detection of the rare-earth ions was 8-quinolinol. The decrease in sensitivity on introduction of a 2-methyl-group on the 8-quinolinol nucleus may be attributed to either a steric hindrance[3] or a solubility effect.

The detection of the rare-earth ions with cupferron compares favorably with 2-methyl-8-quinolinol. However, the tests with cupferron were conducted in neutral solutions. The sensitivity of cupferron to detect the rare-earth ions was much greater than that found for oxalic acid. In fact, of all the reagents studied, oxalic acid was the least sensitive. It is to be expected that the sensitivity of oxalic acid would decrease with increasing hydrogen ion concentration while the sensitivity of the cupferron test would remain about the same.

As a general observation, the sensitivity of the tests decreased with increase in atomic number of the rare-earth metal ion. This decrease in sensitivity is quite prominently shown in going from the lighter[1,2] to the heavier rare-earths.

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[1] W. W. WENDLANDT, *Science*, 125 (1957) 1042.

[2] W. W. WENDLANDT AND D. W. HAYES, *Science*, 126 (1957) 451.

[3] H. IRVING, E. J. BUTLER AND M. F. RING, *J. Chem. Soc.*, (1949) 1489.

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A convenient boiling tube for the safe and steady boiling of solutions

The prolonged boiling of many solutions is often a risky or, at best, a troublesome procedure. Boiling stones, glass beads, marble chips, granules, pebbles, etc., are frequently used in an effort to obtain a more even boiling action and thereby prevent the loss of sample by bumping. However, such devices do not always produce the desired result.

A simple but more effective device for the quiet and safe boiling of solutions, with a minimum amount of manipulation, is a specially-designed boiling tube which may be prepared in any laboratory. Analysts, to whom this accessory has been demonstrated, consider it preeminent as a boiling aid.

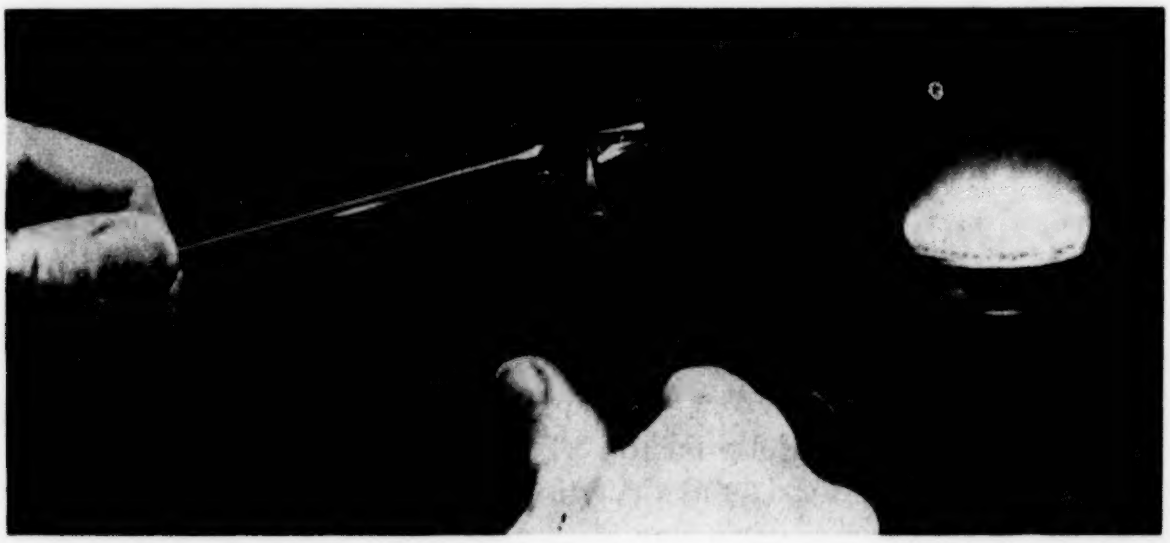

Fig. 1.

Procedure

Obtain a glass tube, preferably one of soft glass, 6 mm in outside diameter and about 8 in. long. After fire-polishing the ends, heat one end until about 1" of it is soft. Immediately thereafter, with the aid of pliers, form a seal by pinching the tube completely closed at one spot about 1/4 in. to 1/2 in. from the heated end (see photograph). Allow the tube to cool.

To use, place the constricted portion of the tube in the solution, touching the edge of the boiling-vessel bottom. A bubble of air should be trapped in the small open section of the tube below the seal. Now heat the solution. When the boiling point is reached, the lower open end of the tube will act as a source from which gases, produced by the boiling, may escape. A very satisfactory boiling action ensues. When the boiling operation is complete, the tube can be easily removed and then rinsed in a matter of seconds.

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HARRY M. PUTSCHÉ

Received March 13th, 1959

REVUE DE LIVRE

Traité de micro-analyse minérale par **Clément Duval**, tome III, 1956, 548 pp., Prix 3,600 Fr., tome IV, 1957, 892 pp., Prix 3,600 Fr., Presses scientifiques internationales, Paris, 1956 et 1957.

Les 4 volumes de ce bel ouvrage sont maintenant sortis de presse. Nous avons déjà présenté le tome I et le tome II. Les tomes III et IV comprennent comme les précédents un élément par chapitre. L'exposé est clair, dans un ordre parfaitement logique, ce qui rend la consultation de ce traité particulièrement agréable et aisée.

Le tome III renferme les éléments des colonnes VIIIa, Ib et IIb du système périodique, soit les éléments de numéro atomique 26 à 30, 44 à 48 et 76 à 80. Au total 15 éléments. Le tome IV traite des éléments des colonnes IIIb, IVb, Vb, VIb, VIIb et o, soit en tout 31 éléments.

L'auteur est bien modeste lorsqu'il intitule son ouvrage: ,,*Traité de micro-analyse minérale*", car, en fait, il a largement dépassé ce cadre et on trouve dans son livre une foule de documents sur tout le domaine de l'analyse minérale. En particulier, il donne de nombreux renseignements sur l'analyse de traces et sur l'ultramicroanalyse.

On ne saurait trop féliciter **Clément Duval** pour le choix des méthodes qu'il nous propose et spécialement de l'énorme travail de bibliographie que lui et ses collaborateurs se sont imposés et grâce auquel cet ouvrage est l'un des plus documentés et des plus complets dans ce domaine de l'analyse. Pour le cobalt, par exemple, on trouve 389 références, 311 pour le nickel, 745 pour le cuivre et ainsi de suite. On comprend dès lors le succès qu'il a rencontré; il rend et rendra à tous ceux qui de près ou de loin s'intéressent à la chimie analytique minérale, les plus grands services)

D. **Monnier** (Genève.

BOOK REVIEW

Precipitation from Homogeneous Solution, by **L. Gordon, M. L. Salutsky and H. H. Willard**. John Wiley & Sons Inc. New York 1959, 187 pages. $ 7.50.

It is refreshing to read a current publication dealing with an important aspect of 'classical' methods of analysis, which tends to confirm that the craftmanship associated with this branch of chemistry has still an important part to play, despite all the recent advances in instrumental method of analysis.

The publication can be divided into two sections, dealing first with practical applications of homogeneous precipitation, then, commencing with Chapter 8, a theoretical approach to the subject is made; the reason for this reversal of customary practice is not obvious.

As a source of reliable information on the subject of homogeneous precipitation, the book can be recommended, but the analyst is invariably left to speculate as to the real purpose for which the recommended procedures are intended. Many of the procedures are inordinately time consuming, e.g. on page 47 the statement is made that 'quantitative precipitation of zirconium requires 18 to 24 hours at the boiling point'; in other instances, procedures can only be applied in the absence of a large range of elements, an ideal state of affairs rarely, if ever, the lot of the analyst. It is difficult to appreciate the value of the recommended method for determining gallium, based on precipitation of what is, presumably, basic gallium sulphate, brought about by the slow hydrolysis of urea, when it is known that many metals are also precipitated under similar conditions. The authors do, however, recommend that the determination of gallium should be completed colorimetrically, but in this, as in other methods, there is no obvious reason why determination of the metal in question should not be made direct in the first instance.

The book is written in a very clear style.

The underlying principle of homogeneous precipitation is governed by the factors embodied in the **von Weirmann** equation and it is disappointing to find that this relatively simple equation does not appear anywhere in the book.

This critical survey should not detract from the value of the adequate coverage the authors have given to the subject of homogeneous precipitation, particularly for the analyst who has a use for this fascinating technique.

W. J. **Elwell** (Birmingham)

BUCHBESPRECHUNG

Qualitative Analyse, von N. I. Blok, VEB, Deutscher Verlag der Wissenschaften, Berlin, 1958, (das Buch ist eine Übersetzung und deutsche Bearbeitung des 1952 in russischer Sprache in Moskau und Leningrad herausgekommenen Buches) 574 S., 59 Abb., 60 Tabellen, DM 36.—.

Bei diesem als Lehrbuch für Studenten gedachten Werk handelt es sich nicht um ein Lehrbuch der praktischen Analyse, wie der Titel vielleicht vermuten läßt. Der ganzen Anlage nach würde ein Titel wie *Einführung in die anorganische und allgemeine Chemie an Hand der chemischen Analyse* dem Inhalt besser gerecht werden. Das Hauptanliegen des Buches ist es, die Grundlagen für einen Unterricht zu geben, bei dem der Student in erster Linie mit den chemischen Eigenschaften der Stoffe in wäßrigen Lösungen bekannt gemacht werden soll. Hierzu wird, wie das seit langem üblich und verbreitet ist, in erster Linie von solchen Reaktionen ausgegangen, die analytisch angewendet werden.

Dasjenige, was das hier vorliegende Buch von vielen Büchern ähnlicher Zielsetzung unterscheidet, ist, daß mit großer Konsequenz versucht worden ist, den Benutzer dadurch zu einem tieferen Verständnis und auch zu einer besseren und leichteren Übersicht zu führen, daß das analytisch Interessierende und das allgemeine chemische Verhalten eines Elementes aus seiner Stellung im Periodischen System, sowie aus Elektronenkonfiguration und Ionenpotential des einzelnen Ions hergeleitet wird, soweit das irgend angängig ist.

Wie aus dem Gesagten hervorgehen dürfte, spielt die theoretische Betrachtung der chemischen Vorgänge eine wesentliche Rolle und nimmt dementsprechend einen relativ breiten Raum ein. Allein der Allgemeinbehandlung der Grundlagen (Periodensystem, Massenwirkungsgesetz, elektrolytische Dissoziation, Löslichkeitsprodukt, Wasserstoffionenkonzentration, Hydrolyse, Puffergemische, Fällungen, Adsorption, Kolloide Lösungen, Mitfällung, Redoxreaktionen, Komplexverbindungen) sind 127 von insgesamt 518 Textseiten gewidmet. Aber auch in den weiteren Kapiteln, in denen die verschiedenen analytischen Gruppen behandelt werden, sind immer wieder theoretische Betrachtungen eingestreut. In dem Abschnitt „Analyse der Kationen" (270 Seiten) sind die Nachweisreaktionen für die Ionen von 31 Elementen angegeben und durchweg unter Angabe der Reaktionsgleichungen erläutert. Eine kurze Skizzierung der wesentlichen chemischen Eigenschaften der Elemente sowei eine allgemeine Charakteristik der einzelnen analytischen Gruppen ist jeweils vorangestellt. Die vielfach als zwei besondere Gruppen betrachteten Elemente der Ammoniak- und Ammoniumsulfidgruppe werden als eine gemeinsame Gruppe behandelt. In den systematischen Trennungsgängen für die Kationen der einzelnen Gruppen ist allerdings nicht auf alle Elemente, deren Nachweisreaktionen angegeben sind, Rücksicht genommen worden. Insofern entsprechen die hier gegebenen Trennungsschemata etwa dem Umfang der einfachen Schulanalyse. Die „Analyse der Anionen" (64 Seiten) behandelt in entsprechender Form die Verhaltensweise und die charakteristischen Reaktionen von 24 Anionen bzw. nichtmetallischen Elementen. In weiteren Kapiteln werden Angaben zur mikrochemischen Kristallanalyse (9 Seiten), zur Tüpfelanalyse (8 Seiten), zur Chromatographie ($1^1/_2$ Seiten) und zur praktischen Durchführung qualitativer Analysen (22 Seiten) gemacht, wobei auch kurz auf die Untersuchung von Metallen, Legierungen und Mineralen eingegangen wird.

In dem Werk ist eine beträchtliche Fülle an Stoff in sehr übersichtlicher und verständlicher Form dargeboten. Man findet ferner viele Zahlenangaben über die Löslichkeiten analytisch interessierender Verbindungen, über Stabilitätskonstanten von Komplexen, Dissoziationskonstanten von Säuren und Basen sowie Redoxpotentiale. Einige kleinere Ungereimtheiten, wie in einzelnen Fällen die Angabe unterschiedlicher Zahlen für ein und dieselbe Größe an verschiedenen Stellen des Buches, werden sich bei einer späteren Auflage sicher beheben lassen.

Ein verständnisvolles Durcharbeiten dieses Buches wird für den Studenten zweifellos von großem Nutzen sein.

H. Bode (Hannover)

ANNOUNCEMENTS

THIRD CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR REACTOR TECHNOLOGY

THE ANALYSIS OF REACTOR MATERIALS FOLLOWING THE OPERATION OF NUCLEAR REACTORS

The Oak Ridge National Laboratory has announced that the Third Conference on Analytical Chemistry in Nuclear Reactor Technology will be held at Gatlinburg, Tennessee, on October 26, 27 and 28, 1959.

The general theme of this conference, analysis of reactor materials following the operation of nuclear reactors, complements sequentially those of prior meetings which dealt with, (1) advances in the chemical analysis of important reactor materials, and (2) the role of analytical chemistry in the startup and operation of nuclear reactors.

The subjects which will be emphasized at this conference are: chemical analysis as related to the estimation of corrosion and erosion rates, reprocessing of fuels and blanket materials, and the analytical chemistry of fission product mixtures, of plubtonium, and of the transplutonic elements.

The contribution of papers pertaining to these or closely related subjects is solicited. Presentations on new developments or improvements in methods of chemical analysis, including advances in instrumentation, are especially invited although review papers and those involving pertinent theoretical discussions may well prove to be of equal interest and should be submitted for consideration.

To facilitate the completion and distribution of the program well in advance of the conference, speakers are requested to submit abstracts of about 500 words not later than August 1, 1959, and to indicate the time required for their presentation, not to exceed 30 min.

The Proceedings of the conference will be published. In order to be included in the Proceedings, manuscripts must be submitted prior to the opening of the conference. Publication in the Proceedings is not mandatory, but desirable. If a paper is not to be published in the Proceedings, the abstract and a reference to another source of publication, if any, will be made.

All communications relative to the conference, including the submission of manuscripts and abstracts, should be directed to: C. D. SUSANO, Oak Ridge National Laboratory, P. O. Box Y, *Oak Ridge*, Tennessee.

Inquiries with respect to accommodations or requests for reservations should be addressed to: Mr. TOM WOODS, Manager Mountain View Hotel, *Gatlinburg*, Tennessee.

Gatlinburg, Tennessee; October 26–28, 1959

TENTATIVE PROGRAM

At this stage in the development of the program, it is indicated that a morning and afternoon session will be held on each of the three days of the conference. If sufficiently greater interest is evidenced in certain aspects of this subject matter, arrangements will be made to increase the number of sessions but within the scheduled period of three days. Every effort will be made to avoid conflicts of interest in scheduling concurrent sessions.

Since it is intended that the scope of the program will necessarily encompass only a limited portion of the field of analytical chemistry as it pertains to the analysis of materials after they have been involved in an operating reactor, the general topics for each of the six sessions will be essentially as follows:

MONDAY, OCTOBER 26

Morning – The Analysis of Spent Reactor Fuels.
Afternoon – Analytical Chemistry of Exposed Blanket Materials.

TUESDAY, OCTOBER 27

Morning – Analytical Chemistry in the Reprocessing of Fuels and Blanket Materials.
Afternoon – The Analysis of Corrosion and Erosion Products.

WEDNESDAY, OCTOBER 28

Morning – The Analysis of Fission Product Mixtures.
Afternoon – Analytical Chemistry of Plutonium and Transplutonic Elements.

In addition to the formal technical program, an informal dinner and dance will be held on Tuesday evening. Arrangements are now being made to secure a prominent speaker, particularly in the field of analytical chemistry or some closely related field, to address the group after the dinner.

The conference is being conducted on an unclassified basis and all interested persons, regardless of affiliation, are invited to attend or participate in all or any portion of the meeting.

There will be no registration fee but, however, for those who partake of the dinner, a nominal charge will be made.

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY

Starting with the January, 1959 issue, The Chemical Society is to publish, with the support of the Department of Scientific and Industrial Research, a cover-to-cover translation of the monthly journal, *Zhurnal neorganicheskoĭ Khimii*, a publication of the Academy of Sciences of the U.S.S.R. The translation will be undertaken for the Society by Infosearch Ltd., and the Society has appointed Professor P. L. ROBINSON as Executive Editor of the publication. Professor Robinson will be assisted by an advisory panel of distinguished inorganic chemists.

The sale and distribution of the journal will be undertaken by Cleaver-Hume Press Ltd., 31 Wright's Lane, London, W.8, from whom a detailed prospectus giving the scope of this journal may be obtained.

Translations will be issued in monthly parts as soon as possible after the Russian original is available. The subscription rate will be £ 30 (U.S.A. $ 90) per annum, but Universities and Technical Colleges may subscribe at a discount of 25%. Single issues can be purchased at £ 4 (U.S.A. $ 12) per copy to all purchasers.

The Society also hopes to start the publication within the next year of translations of the Russian "*Journal of Physical Chemistry*" (*Zhurnal fizicheskoĭ Khimii*) and "*Progress in Chemistry*" (*Uspekhi Khimii*).

THE SPECTROPHOTOMETRIC DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS. II

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INTRODUCTION

Some recent advances and improvements in this well established technique were described in a previous paper[1], which should be regarded as part I of this series. The techniques described therein have been used many times and have proved satisfactory. The object of the present paper is to provide data calculated from measurements of the unique range of spectra of the pure hydrocarbons employed in the previous investigation, which can be of use in routine analysis of complex mixtures of these hydrocarbons.

It is well known that in many combustion products, quantitative separation of the polycyclic aromatic hydrocarbons from each other is very difficult and in some cases impossible. Nevertheless, satisfactory determinations have been made by measuring the heights of absorption peaks characteristic of individual compounds in incompletely separated fractions.

EXPERIMENTAL

Full details of experimental procedure have been given in the previous paper for which a number of spectra were prepared which have been employed in the present investigation. Additional spectra were also prepared for the present work and one additional compound, 1 : 2, 3 : 4-dibenzpyrene, has been examined. The absorption peak heights were measured from tangents drawn to the minima on each side of the peak; the "base-line" technique[2,3]. In the previous paper tables of absorbances (optical densities) were given for use with completely separated individuals but if the base-line technique is employed it is necessary to refer to calibration tables of heights measured in this way from standard spectra of pure compounds.

Table I is a list, arranged in chromatographic sequence, of the heights (in terms of O.D. or absorbance per μg per ml) so measured for a number of the more prominent absorption peaks. The spectra were determined in 1-cm silica cells as in the previous paper by means of a Beckman D.K.2 ratio-recording spectrophotometer.

In scanning spectra for identification of individual compounds a list of prominent peaks in wavelength order with the compounds corresponding to them is also of great value. Such a list is compiled in Table II.

During the compilation of these data an attempt was made to separate two isomeric dibenzpyrenes by repetitive alumina chromatography. A mixture of 1 : 2, 3 : 4- and 3 : 4, 9 : 10-dibenzpyrenes was not separated after passing through three successive columns, although the 3 : 4, 9 : 10-isomer appeared to be slightly more readily

TABLE I

CHROMATOGRAPHIC SEQUENCE OF ELUTION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM ACTIVE ALUMINA COLUMNS WITH CYCLOHEXANE

Compound	*Wavelength of peaks*	*Base-line factor (optical density for 1 μg/ml)*
Naphthalene	311	0.00156
Azulene	341	0.0194
	353	0.00807
2-Methylnaphthalene	305	0.00136
	320	0.00258
Acenaphthene	288	0.0127
	300	0.00815
	307	0.00734
	321	0.00942
Acenaphthylene	323	0.0255
	335	0.0097
	340	0.0184
Fluorene	221	no base to peak
	265	0.106
	301	0.0515
Phenanthrene	252	0.341
	293	0.0725
Anthracene	253	0.925
	340	0.0191
	357	0.0386
	376	0.0460
Pyrene	273	0.242
	320	0.117
	335	0.278
Fluoranthene	237	0.180
	288	0.222
3-Methylpyrene	243	0.268
	276	0.224
	344	0.181
1 : 2, 3 : 4-Dibenzanthracene	323	0.0014
	333	0.00516
	350	0.00812
1 : 2-Benzanthracene	278	0.188
	289	0.346
Chrysene	269	0.524
	294	0.0160
	306	0.0277
	320	0.0456
Naphthacene	441	0.0372
	471	0.0472
Perylene	253	0.0920
	409	0.0590
	437	0.119

TABLE I (continued)

Compound	*Wavelenght of peaks*	*Base-line factor (optical density for 1 μg/ml)*
1 : 2-Benzpyrene	278	0.131
	290	0.168
	317	0.0500
	332	0.138
3 : 4-Benzpyrene	266	0.147
	285	0.164
	297	0.260
	364	0.0618
	385	0.101
	404	0.0164
1 : 12-Benzperylene	289	0.0640
	300	0.149
	363	0.0470
	384	0.0805
Anthanthrene	233	0.146
	307	0.242
	430	0.232
Coronene	302	0.668
	339	0.166
3 : 4, 9 : 10-Dibenzpyrene	242	0.234
	295	0.186
	372	0.148
	394	0.262
1 : 2, 3 : 4-Dibenzpyrene	290	0.0228
	331	0.0557
	401	0.0182

TABLE II

Wavelength	*Compound*	*Wavelength*	*Compound*
471	Naphthacene	350	1 : 2, 3 : 4-Dibenzanthracene
441	Naphthacene	344	3-Methylpyrene
437	Perylene	341	Azulene
430	Anthanthrene	340	Acenaphthylene, Anthracene
409	Perylene	339	Coronene
404	3 : 4-Benzpyrene	335	Acenaphthylene, Pyrene
401	1 : 2, 3 : 4-Dibenzpyrene	333	1 : 2, 3 : 4-Dibenzanthracene
394	3 : 4, 9 : 10-Dibenzpyrene	332	1 : 2-Benzpyrene
385	3 : 4-Benzpyrene	331	1 : 2, 3 : 4-Dibenzpyrene
384	1 : 12-Benzperylene	323	Acenaphthylene, 1 : 2, 3 : 4-Dibenzanthracene
380	Anthanthrene	321	Acenaphthene
376	Anthracene	320	2-Methylnaphthalene, Pyrene, Chrysene
372	3 : 4, 9 : 10-Dibenzpyrene	317	1 : 2-Benzpyrene
364	3 : 4-Benzpyrene		
363	1 : 12-Benzperylene		
357	Anthracene		
353	Azulene		

TABLE II (continued)

Wavelength	*Compound*	*Wavelength*	*Compound*
311	Naphthalene	278	1 : 2-Benzanthracene, 1 : 2-Benzpyrene
307	Acenaphthene, Anthanthrene	276	3-Methylpyrene
306	Chrysene	273	Pyrene
305	2-Methylnaphthalene	270	Naphthacene
302	Coronene	269	Chrysene
301	Fluorene	266	3 : 4-Benzpyrene
300	Acenaphthene, 1 : 12-Benzperylene	265	Fluorene
297	3 : 4-Benzpyrene	261	Benzene
295	3 : 4, 9 : 10-Dibenzpyrene	255	Benzene
294	Chrysene	253	Anthracene, Perylene
293	Phenanthrene	252	Phenanthrene
290	1 : 2-Benzpyrene, 1 : 2, 3 : 4-Dibenzpyrene	249	Benzene
289	1 : 2-Benzanthracene, 1 : 12-Benzperylene	243	3-Methylpyrene
288	Acenaphthene, Fluoranthene	242	3 : 4, 9 : 10-Dibenzpyrene
285	3 : 4-Benzpyrene	237	Fluoranthene
		233	Anthanthrene
		221	Fluorene

eluted. It is therefore unlikely that these two compounds will be separable from mixtures containing them both, but they can be recognised when present together.

It should be noted that use of the factors given in the tables can provide in many cases only approximately quantitative amounts, and that the accuracy is improved with solutions containing fewer constituents. However, with repetitive determinations on a large number of samples, the approximate method is much faster and gives useful comparative results.

ACKNOWLEDGEMENT

The author thanks the Medical Research Council for supporting this investigation by the loan of equipment and provision of technical assistance.

SUMMARY

In repetitive determinations of polycyclic aromatic hydrocarbons in combustion products the use of incompletely separated chromatographic fractions is often an advantage favouring rapid work. Such fractions may be submitted to an approximate quantitative analysis by using tables of absorption peak heights measured from a base-line drawn between the minima on each side of the peak. Convenient tables for this method are provided in this paper.

RÉSUMÉ

Lors des dosages d'hydrocarbures aromatiques polycycliques dans des produits de combustion, il est souvent plus avantageux d'utiliser des fractions chromatographiques, incomplètement séparées. Des tables sont proposées pour effectuer cette détermination.

ZUSAMMENFASSUNG

Die Serien-Bestimmungen von polyclischen aromatischen Kohlenwasserstoffen in Verbrennungsprodukten durch chromatographische Trennung können oft rascher durchgeführt werden, wenn hierzu nicht-vollständig getrennte chromatographische Fraktionen verwendet werden. Eine angenähert quantitative Auswertung der Ergebnisse kann mit Hilfe der gegebenen Tabellen erfolgen.

REFERENCES

[1] A. J. Lindsey, *Anal. Chim. Acta,* 20 (1959) 175.
[2] R. L. Cooper, *Analyst,* 79 (1954) 573.
[3] B. T. Commins, *Analyst,* 83 (1958) 886.

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A SYSTEMATIC SCHEME OF QUALITATIVE ANALYSIS FOR ANIONS. IV

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A systematic scheme[1,2] of qualitative analysis for anions has been put forward from this laboratory. In the first paper it was pointed out that there are three problems (a), (b) and (c) that must be investigated carefully, if the sodium carbonate filtrate is to be used for the systematic separation of anions into groups in a satisfactory manner. This paper embodies the results of investigating problem (b) in a systematic manner. It has been found that the number of elements that pass into the 10% sodium carbonate filtrate is very much larger than is usually supposed, though the amounts of many elements present under ordinary circumstances are small. Luckily the presence of these elements in this filtrate does not interfere with the detection of the anions and the scheme that has been worked out remains practically unaltered as far as the detection of anions is concerned.

The present investigation has enabled us not only to get a clear picture of the distribution of the basic radicals in the different groups, but also to provide for their detection, if necessary, without interfering with the detection of the anions. If the sodium carbonate filtrate is to be tested for the anions only, the tests for the basic radicals can be omitted. If on the other hand the sodium carbonate filtrate is to be used for the detection of both basic radicals and anions, the tests for the basic radicals can be applied in addition to those for the anions. It can, however, be seen from Table I that under certain circumstances some basic radicals (Pt, Ru, Ph, Ga, Ge, Tl^+, Re), which are tested for in the solution prepared with conc. HNO_3 and HCl, may pass completely into the sodium carbonate filtrate, and to ensure their detection it is necessary to test for them in this filtrate also.

A detailed knowledge of the distribution of both basic radicals and anions in the sodium carbonate filtrate is especially necessary, if a systematic and integrated scheme for the detection of basic radicals, anions and insoluble substances is to be worked out. The possibilities of devising such a comprehensive scheme are being explored in this laboratory and it is hoped that with the completion of this work it will be possible to evolve an integrated scheme according to the procedure given on page 109.

A general idea of the elements that pass into the sodium carbonate filtrate and their distribution in the different groups will be obtained from Table I. This table is the same in general outline as Table I of Part I, but differs from it in having a larger number of basic radicals in some groups. All the basic radicals that may be present with the anions are shown in this table, but those that partially pass into the sodium carbonate filtrate are printed in bold-face type. To avoid repetition the anions of the groups have not been given. In order to provide for the detection of basic radicals as well as anions in the sodium carbonate filtrate, some modifications had to be intro-

TABLE I

Sodium carbonate filtrate containing all the anions and some basic radicals. Treat with sufficient excess of $PbCO_3$ and filter

Ppt.
Anions of the group + **Ce, Hg, Ir, Os,** Ru and Rh.
See Table II

Filt.
Rest of the anions + **Al, Be, Cu, Co, Ni, U, Ti, Fe^{+2},** (**Hg**), **Ce,** (**Ir**), **Au, Th, Zr,** Pt, Ga, Ge, (Ru), (**Os**), (Rh), Tl^+, Re and rare earths.
Treat with excess of $Zn(NO_3)_2$ or $Zn\ (CH_3COO)_2$ and filter

Ppt.
Anions of the group, $ZnCO_3$ + **Al, Be, Cu, Co, Ni, U, Ti, Fe^{+2},** (**Hg**), **Ce,** (**Ir**), **Au, Th, Zr,** Pt, Ga, Ge, (Ru), (**Os**) and (Rh) + (rare earths). Treat with excess of dil. NH_4OH and filter

Filt.
Rest of the anions + **Au,** traces of **Be, Co, Ni,** (rare earths) + (AsO_3^{-3}), Tl^+ and Re.

Proceed as shown in Table I of ref.[1], first testing for Au in a portion of the filtrate with NaOH and Na_2O_2

Ppt.
Anions of the group + **Al, Be, Ce,** (**Ir**), **Tl, Fe^{+2}, Zr, Th,** Ru and (Rh) + (rare earths).
See Table III

Filt.
Rest of the anions + **Al, Be, Cu, Co, Ni, U,** (**Hg**), (**Ir**), Pt, Ga, Ge, (**Os**) and (Rh).
Add magnesia mixture and conc. NH_4OH, heat and filter

Ppt.
Anions of the group + **Al, Be,** Pt, Ga and Ge.
See Table IV

Filt.
Rest of the anions + **Cu, Co, Ni, U,** (**Hg**), (**Ir**), (**Os**) and (Rh).
Add $Ca\ (NO_3)_2$ and $Ba(NO_3)_2$ and filter

Ppt.
Anions of the group

Filt.
Anions of the group + **Cu, Co, Ni, U,** (**Hg**), (**Ir**), (**Os**) and (Rh).

See Table III of ref.[2]

TABLE II

<table>
<tr><td colspan="7">Lead salts of the group anions + **Os,** Ru, Rh, **Ce, Hg, Ir** and $PbCO_3$. If the precipitate is black or grey in colour, test a portion for sulphide with Zn and conc. HCl. Dissolve the precipitate in dil. HNO_3, distil the solution with conc. HNO_3 and collect the distillate in 6 *N* NaOH solution</td></tr>
<tr><td colspan="6">Res. Nitrates of Ru, Rh, Ce, Hg, Ir and Pb. Add 2–3 g of $KBrO_3$ and distil again, collect the distillate in a hot solution of $Ba(OH)_2$</td><td rowspan="6">Dist. Yellow to red solution of sodium osmate. Acidify with HCl and test for Os with KCNS and ether or thio-urea</td></tr>
<tr><td colspan="5">Res. Nitrates of Rh, Ce, Hg, Ir and Pb. Evaporate almost to dryness, take up the residue with dil. HCl and filter</td><td rowspan="5">Dist. Heat to boiling and filter off barium ruthenate. Dissolve the precipitate in HCl and test for Ru with thio-urea</td></tr>
<tr><td rowspan="4">Ppt.
$PbCl_2$
Reject.</td><td colspan="4">Filt. Chlorides of Rh, Ce, Hg, Ir and (Pb). Add freshly prepared 2 <i>N</i> Na_2S reagent in excess followed by an equal vol. of conc. HCl and 2–3 g of ammonium acetate. Heat to boiling and filter</td></tr>
<tr><td colspan="3">Ppt. Sulphides of Rh, Hg, Ir and (V). Treat with excess of Na_2S reagent and filter</td><td rowspan="3">Filt.
Chlorides of V, Ce and (Pb).
Boil to remove H_2S and test for V with H_2O_2.
Add NaOH solution in excess to the same solution and heat to boiling.
A yellow precipitate confirms Ce</td></tr>
<tr><td rowspan="2">Ppt. Rh_2S_3, confirm as usual.
<i>Note</i>:
Precipitated Rh_2S_3 like Re_2S_7 does not dissolve in Na_2S reagent</td><td colspan="2">Filt. Thiosalts of Hg, Ir and (V). Add 2–3 g of ammonium acetate and filter.</td></tr>
<tr><td>Ppt.
HgS.
Confirm as usual</td><td>Filt. Thiosalts of Ir and (V).
Test as usual</td></tr>
</table>

TABLE III

<table>
<tr><td colspan="4">Ppt. Zinc salts of the group anions + Zr, Th, Al, Be, Ti, Fe^{+2}, Ce, (Ru), (rare earths) and traces of Rh, Ir, Au°. Treat with excess of NaOH solution and filter</td></tr>
<tr><td colspan="2">Ppt. Au°, hydroxides and phosphates of Zr, Th, Ti, Ce, Fe^{+2} (rare earths).
Treat with dil. HNO_3 and filter</td><td colspan="2">Filt. Zn^{+} rest of the anions + Al, Be, (Ru) and traces of Rh and Ir.
Acidify with dil. HCl and filter</td></tr>
<tr><td>Ppt.
Zr$(HPO_4)_2$ and Au°.
Test as usual for Zr and PO_4^{-3}</td><td>Filt. Th, PO_4^{-3}, Zr, Fe^{+2}, Ti, Ce and (rare earths).
Test as usual for cations and PO_4^{-3} (Tables VI and VIII of ref.[4])</td><td>Ppt.
$Zn_2Fe(CN)_6$</td><td>Filt. Zn + rest of the anions + Al, Be, (Ru) and traces of Rh and Ir.
(a) Test a portion for IO_4^- as usual (Table I of ref.[2]).
(b) Distil the remaining portion with conc. HNO_3 + $KBrO_3$ and test the distillate for Ru. Evaporate the remaining solution to dryness, take up the residue with HCl and test for remaining anions and basic radicals as usual (Table I of ref.[2])
The traces of Rh and Ir present here need not be tested for</td></tr>
</table>

TABLE IV

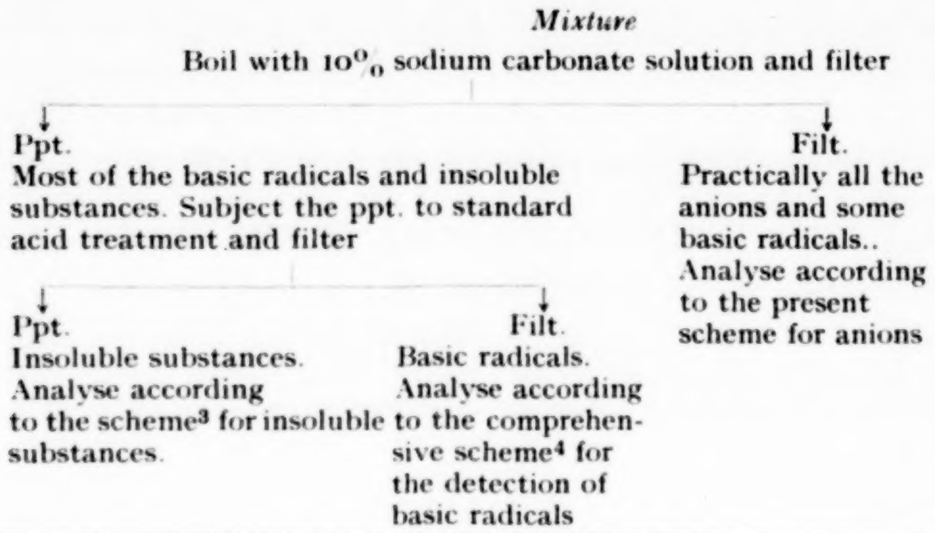
<table>
<tr><td colspan="5">Ppt. Magnium salts of AsO_4^{-3}, AsO_3^{-3}, PO_4^{-3}, PO_3^{-3}, TeO_3^{-2}, (F^-), SiO_3^{-2}, SbO_4^{-3}, SbO_3^{-3} [a] and SnO_3^{-2} [b] + Al, Be, Pt, Ga and Ge.
Treat with excess of dil. CH_3COOH and filter</td></tr>
<tr><td colspan="2">Ppt. TeO_3^{-2}, (AlPO_4), phosphate and arsenite of Ga + Pt.
Dissolve in dil. HCl. Add excess of freshly prepared 2 <i>N</i> Na_2S reagent followed by an equal vol. of conc. HCl. Heat to boiling and filter</td><td colspan="3">Filt. Rest of the anions + Al, Be, (Pt), Ga and Ge.
Add $Ca(NO_3)_2$ solution in slight excess and filter</td></tr>
<tr><td rowspan="2">Ppt. sulphides of Pt, Te and As.
Test as usual (Table II of ref.[4])</td><td rowspan="2">Filt. PO_4^{-3}, chlorides of Ga and (Al).
Test for Ga with $K_4Fe(CN)_6$ and for PO_4^{-3} with ammonium molybdate</td><td rowspan="2">Ppt.
CaF_2</td><td colspan="2">Filt. Rest of the anions + Al, Be, (Pt), Ge and Ga.
(a) Add sodium phosphate to a portion and if any precipitate is obtained, test it for Ga.
(b) Neutralize the excess of acid with NaOH and then add freshly prepared 1 <i>N</i> Na_2S in excess and filter</td></tr>
<tr><td>Ppt. Anions of the group + Al, Be, Ca and Mg.
Test as usual (Table II of ref.[2])</td><td>Filt. Thiosalts of the anions + (Pt), Ge and Ga.
Proceed as indicated previously (Table II of ref.[2]), testing for Ge in the precipitate of As_2S_3, TeS_2 by distillation with HCl + $KClO_3$.
Traces of Pt need not be tested for</td></tr>
</table>

[a] In Table I of part I and Table II of part II SbO_3^{-3} has inadvertently been given as SbO_2^{-2} in some places.

[b] All the tin is present here in the form of stannate. In previous papers[1,2] the presence of stannite in this precipitate has mistakenly been indicated.

TABLE V

<table>
<tr><td colspan="4">Filtrate from $Ba(NO_3)_2$, containing the rest of the anions + basic radicals shown previously (Table V of ref.[2]), (AsO_3^{-3}), Tl^+, Re.
Add $AgNO_3$ solution in slight excess boil for 2–3 min and filter</td></tr>
<tr><td colspan="2">Ppt. AgCl, AgBr, AgI, AgCNS, $AgIO_3$, Ag_2S, Ag_3PO_4 (from PO_2^{-3}) (Ag_3AsO_3).
Treat with dil. HNO_3 and filter</td><td colspan="2">Filt. Rest of the anions + Be, (Cd, Ca, Ba), Tl^+, Re. Boil with a slight excess of Na_2CO_3, filter and reject the precipitate. Treat the filtrate as indicated previously (Table V of ref.[2]), to test for ClO_3^- and BrO_3^- as AgCl and AgBr. In the filtrate neutralize the acid with NaOH and add excess of Na_2S reagent and filter</td></tr>
<tr><td>Ppt. AgCl, AgBr, AgI, AgCNS, $AgIO_3$.
Test as usual Table V of ref.[2])</td><td>Filt. $AgNO_3$
PO_4^{-3}, (AsO_3^{-3}).
Test as usual</td><td>Ppt. Sulphides of Ag, Mn and Tl.
Test for Tl as usual</td><td>Filt. ClO_4^- and thiosalt of Re.
(a) To a portion of the filtrate add an equal vol. of conc. HCl and 2–3 g of ammonium sulphate. Heat to boiling. A black ppt. confirms Re.
(b) Acidify another portion with dil. H_2SO_4 and test for ClO_4^- as indicated previously (Table V of ref.[2])</td></tr>
</table>


Mixture
Boil with 10% sodium carbonate solution and filter
Ppt.
Most of the basic radicals and insoluble substances. Subject the ppt. to standard acid treatment and filter
Filt.
Practically all the anions and some basic radicals.. Analyse according to the present scheme for anions
Ppt.
Insoluble substances. Analyse according to the scheme[3] for insoluble substances.
Filt.
Basic radicals. Analyse according to the comprehensive scheme[4] for the detection of basic radicals

duced into the detailed analysis of the groups. These modifications will be clear from the tables.

The solubility of the rare earths in the sodium carbonate filtrate was in general found to increase with increasing atomic weight of the element; the first few rare earths (with the exception of cerium) are practically insoluble in the sodium carbonate solution, whereas those at the end of the series are completely soluble. The rare earths that dissolve in 10% sodium carbonate solution are precipitated almost completely by zinc acetate and are found together with Zr, Th, etc., as shown in Table III. The small amounts of the rare earths that pass into the filtrate after precipitation with zinc acetate are precipitated with the sodium sulphide reagent used in the last step of the group analysis (Table V) along with the sulphides of Ag, Mn, Tl, etc.

ACKNOWLEDGEMENT

The authors express their gratitude to the Scientific Research Committee, U.P.-Government, for granting a research assistantship to one of them (M. LAL).

SUMMARY

A comprehensive investigation has been undertaken to ascertain how the basic radicals that pass into the sodium carbonate filtrate are distributed among the various groups for the detection of anions. Methods for the detection of these basic radicals in the presence of the anions have been worked out in detail. It was found that the scheme for the detection of anions put forward previously remains unaffected by the presence of these basic radicals. It has been shown that the scheme for the detection of anions can be integrated with the comprehensive schemes for the detection of basic radicals and insoluble substances.

RÉSUMÉ

Une étude a été effectuée pour déterminer la répartition des radicaux basiques (obtenus par traitement au carbonate de sodium), dans les divers groupes de l'analyse des anions. L'auteur décrit aussi les méthodes d'identification de ces radicaux, en présence des anions.

ZUSAMMENFASSUNG

Es wird die Verteilung basischer Radikale in den einzelnen Gruppen der Anionen nach der Behandlung mit Natriumcarbonat untersucht. Die Identifizierung dieser Radikale neben den Anionen wird beschrieben.

REFERENCES

[1] I. K. TAIMNI AND MANOHAR LAL, *Anal. Chim. Acta*, 17 (1957) 367.
[2] I. K. TAIMNI AND MANOHAR LAL, *Anal. Chim. Acta*, 17 (1957) 372.
[3] G. B. S. SALARIA, *Anal. Chim. Acta*, 19 (1958) 316.
[4] G. B. S. SALARIA, *Anal. Chim. Acta*, 16 (1957) 509.

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SEPARATIONS INVOLVING SULPHIDES

X. SEPARATION OF ZINC FROM SOME ELEMENTS THAT FORM THIOSALTS

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The separation of zinc from other elements which form insoluble sulphides is attained with difficulty because of the solubility of zinc sulphide in dilute hydrochloric acid and its insolubility in acetic acid. It can be separated easily only from those elements whose sulphides are insoluble in fairly strong solutions of hydrochloric acid. In the present investigation, the separation of zinc from some elements which form thiosalts is discussed. The general method adopted was to treat the solution containing the two metals with sodium sulphide reagent and hydrochloric acid. The sulphide of the element was filtered off, weighed after washing and the zinc in the filtrate was estimated as zinc ammonium phosphate.

EXPERIMENTAL

Separation of arsenic, antimony, tellurium, selenium, molybdenum, mercury, gold, platinum or rhenium from zinc.

Standard solutions of sodium arsenate, antimony potassium tartrate, potassium tellurite, selenious acid, ammonium molybdate, mercuric chloride, auric chloride, platinum chloride or potassium perrhenate and zinc chloride (by dissolving zinc oxide in the minimum quantity of dilute hydrochloric acid) were used. Measured volumes of the two solutions were mixed together and subsequently treated with $2N$ sodium sulphide reagent in excess. The mixture containing the thiosalt and zinc sulphide was acidified with a measured quantity of hydrochloric acid. and then heated to boiling and allowed to cool to room temperature. The precipitate was filtered through a weighed sintered glass crucible (porosity 4) and the precipitated metals were estimated as As_2S_5[1], Sb_2S_3[2], TeS_2[1], SeS_2[1], $MoS_3 \cdot 2\,H_2O$[3], HgS[4], Au_2S_3[2], $PtS_2 \cdot 3\,H_2O$[5] or Re_2S_7[4] respectively.

The following points are to be observed in precipitating the sulphides.

1. If a white precipitate appears on mixing the two solutions, it should be dissolved in the minimum quantity of caustic soda.

2. In the case of mercury, the mixture should be first treated with ammonium hydroxide till a white turbidity appears.

3. The solution containing the thiosalt of arsenic, platinum or rhenium should be acidified with a measured quantity of concentrated hydrochloric acid to produce an acidity of approximately $6\,N$ in the resultant mixture. In the case of other elements, the thiosalt is acidified with $2\,N$ hydrochloric acid to produce an acidity of approximately $1\,N$ in the final mixture.

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4. In the case of platinum, the mixture after acidification should be treated with 10–15 g of ammonium acetate; in the case of rhenium, 10–15 g of ammonium sulphate should be used.

After filtration and removal of the sulphide, the filtrate was evaporated to about 50 ml to remove hydrogen sulphide, diluted to 250 ml and zinc was estimated as $ZnNH_4PO_4$[6].

31–39 mg of arsenic, 48–62 mg of antimony, 55–69 mg of tellurium, 42–53 mg of selenium, 42–53 mg of molybdenum, 68–85 mg of mercury or 9–12 mg of gold were separated from 32–39 mg of zinc; 35–44 mg of platinum or 56–57 mg of rhenium were separated from 47–48 mg of zinc.

RESULTS

The metals were recovered with an accuracy of

As 0.0% to −0.3% and Zn + 0.46% to −0.23%
Sb + 0.29% to −0.23% and Zn + 0.23% to −0.18%
Te 0.0% to −0.38% and Zn + 0.46% to 0.0%
Se ± 0.2% and Zn + 0.37% to −0.46%
Mo + 0.15% to 0.0% and Zn + 0.18% to −0.46%
Hg + 0.4% to 0.0% and Zn + 0.18% to −0.23%
Au 0.0% and Zn + 0.37% to −0.46%
Pt 0.0% to −0.2% and Zn 0.0% to −0.46%
Re + 0.22% to 0.0% and Zn + 0.46% to 0.0%

SUMMARY

It has been shown that 2 *N* sodium sulphide reagent can be used for separating arsenic, antimony, tellurium, selenium, molybdenum, mercury, gold, platinum or rhenium from zinc.

RÉSUMÉ

On a pu séparer quantitativement le zinc d'avec l'arsenic, l'antimoine, le tellure, le sélénium, le molybdène, le mercure, l'or, le platine ou le rhénium au moyen d'une solution 2 *N* de sulfure de sodium.

ZUSAMMENFASSUNG

Zink lässt sich mit Hilfe einer 2 *N* Natriumsulfidlösung von Arsen, Antimon, Tellur, Selen, Molybdän, Quecksilber, Gold, Platin oder Rhenium quantitativ trennen.

REFERENCES

[1] I. K. Taimni and R. P. Agarwal, *Anal. Chim. Acta*, 9 (1953) 121.
[2] I. K. Taimni and R. P. Agarwal, *Anal. Chim. Acta*, 10 (1954) 312.
[3] I. K. Taimni and R. P. Agarwal, *Anal. Chim. Acta*, 9 (1953) 203.
[4] I. K. Taimni and G. B. S. Salaria, *Anal. Chim. Acta*, 12 (1955) 519.
[5] G. B. S. Salaria, *Anal. Chim. Acta*, 17 (1957) 395.
[6] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffmann, *Applied Inorganic Analysis*, John Wiley and Sons, New York, 1953, p. 432.

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THERMOMETRIC TITRATION OF URANIUM(IV) WITH POTASSIUM DICHROMATE

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INTRODUCTION

Thermometric methods of analysis have been known to analytical chemists since the pioneer work of DUTOIT AND GROBET[1]. More recently MÜLLER[2] suggested the use of a thermistor as a heat-sensitive device to replace the Beckman thermometer that is still being used by some workers. LINDE *et al.*[3] adapted a thermistor for use in automatic thermometric titrations. JORDAN AND ALLEMAN[4] followed up the work of LINDE *et al.* by determining heats of chelation by thermometric titrations. JORDAN AND ALLEMAN[4] have preferred to call the technique "enthalpymetric" titration as being a term which has greater relation to the fundamental, thermodynamic quantities upon which the technique is based. Their argument is based upon the equation.

$$\Delta H = \Delta F - T\Delta S$$

ΔH = enthalpy change, cal/mole

ΔF = free energy change, cal/mole

T = temperature, °K and

ΔS = entropy change, cal/mole.

The equation indicates that a thermometric titration is sensitive not only to a reaction in which there is a change in free energy but also to one in which the entropy change is significantly large although the free-energy change is small. Accordingly, consideration given to available thermodynamic data may often determine the feasibility of a thermometric titration without experimental work.

The application of the thermometric method to redox titrations was suggested in the article by LINDE *et al.*[3] One of the titrations which appeared feasible was the thermometric titration of uranium(IV) with potassium dichromate.

KOLTHOFF AND LINGANE[5] appear to be the first to have recommended the use of potassium dichromate as a reagent for the quantitative oxidation of uranium(IV) to uranium(VI). Diphenylamine sulfonate may be used as the indicator. Either diphenylamine or diphenylbenzidine, each with the addition of some ferric iron to the solution, is also satisfactory. The dichromate titration of uranium(IV) is now well known. The potentiometric method of titration in which a noble-metal, indicator electrode and any one of various reference electrodes are used is a commonly accepted method of titration.

The electrode mechanism involving dichromate with a bright platinum electrode is not well understood. There is a variance in observed potential with a change in pH of the solution[6]. In addition, from the authors' experience, the platinum electrode, when used as an indicator electrode in redox titrations in the presence of chromium ion, required frequent cleaning and treatment. In some cases after protracted use in solutions containing chromium ions, cleaning of the electrode failed to restore it and replacement was necessary.

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* Operated by Union Carbide Corporation for the Atomic Energy Commission.

EXPERIMENTAL

The experimental arrangement was essentially that suggested by LINDE, ROGERS AND HUME[3] and used later by JORDAN AND ALLEMAN[4]. The required equipment was as follows:

Microburet; constant-speed, syringe-type, 1-ml capacity, made by the Greiner Co. The microburet was driven by a constant-speed motor, available from the Bodine Co., through a gear arrangement.

Stirring motor; 1600-r.p.m., constant-speed, available from the A. S. LaPine Co. Only the slow-speed shaft that operates at a 5.3-reduction of the 1600-r.p.m. shaft was used. The stirring blade was a spiral made of a flattened piece of pyrex glass attached to a pyrex glass rod. The spiral design provides stirring in a vertical as well as a horizontal plane.

Dewar Flask; 250-ml, to provide adiabatic conditions for the titration. A cork stopper bored so as to centre a 20-ml beaker was inserted in the bottom of the flask. The flask closure was a 3-hole cork stopper that provided access for the buret tip, the stirrer shaft, and the glass tube that supported the thermistor.

Thermistor and Recorder. A thermistor was used as a temperature-sensing device. Since a thermistor is essentially a nonlinear resistance element that changes resistance with temperature, it was coupled as an element of a Wheatstone bridge, to which a potential of 1.5 V was supplied by a dry-cell battery. The unbalance potential of the bridge was fed to a Brown recording potentiometer that was set to read 5 mV at full scale. Because the chart paper of the recorder is driven at a constant rate, a direct calibration was made between the inches of chart travel and volume of titrant added by the constant-speed microburet.

The procedure for carrying out the titration was as follows: Five ml of 1.0 N H_2SO_4 solution was pipeted into a 10-ml polyethylene beaker. Test solution was added, but the total volume was not allowed to exceed 6 ml. The beaker was placed in the Dewar flask. The Dewar flask was placed in position on the ring stand and was clamped there. The stirring motor was started and a short interval of time was allowed for thermal equilibration. The Brown recorder was started

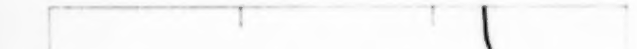

Fig. 1. Typical titration curve.

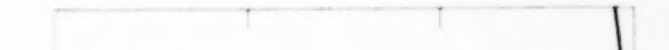

Fig. 2. Titration curve for simulated sample solution.

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and standardized. The thermistor bridge was turned on. The buret drive was started, and the recorder chart was marked simultaneously to show the starting point of the titration. After the termination of the titration, the first two legs of the curve that was plotted on the recorder chart were extrapolated to their point of intersection. The distance from the starting point to the point of intersection was a measure of the volume of titrant required to complete the titration (Fig. 1).

The titrant that was used in the series of titrations under discussion was 1.0 *N* potassium dichromate and was prepared by weighing out primary standard potassium dichromate. The diluent was 1.0 *N* H_2SO_4 solution prepared by the dilution of analytical reagent-grade concentrated sulfuric acid.

DISCUSSION

It has been stated[3] that a redox titration can be followed by the measurement of the heat change involved in the reaction. Accordingly, an investigation, described herein, of the thermometric titration of uranium(IV) with potassium dichromate in solutions that contain uranium(IV), zirconium(IV), aluminium(III), fluoride, chloride, and sulfate ions has shown that the titration is feasible (Fig. 2).

The results of a series of titrations are presented in Tables I and II that follow.

TABLE I

RESULTS OF THE TITRATION OF URANIUM TETRACHLORIDE

Titrant: 1.0 *N* $K_2Cr_2O_7$. Sample solution: UCl_4 in HCl solution; 108 mg of U(IV)/ml. Diluent: 1.0 *N* H_2SO_4 solution. Volume of test portion: 0.10 ml. Chart calibration: 1 inch of chart travel ≎ 0.0162 mequiv.

Test No.	*Chart travel inches*
1	5.60
2	5.60
3	5.62
4	5.60
5	5.62
Average	5.61

Relative standard error at 95% probability level = ±0.25%

TABLE II

RESULTS OF TITRATION OF SOLUTIONS OF URANIUM TETRACHLORIDE THAT CONTAINED SODIUM FLUORIDE AND ALUMINIUM CHLORIDE

Titrant: 1.0 *N* $K_2Cr_2O_7$. Sample solution: UCl_4 in HCl solution, 108 mg of U(IV)/ml. Diluent: 1.0 *N* H_2SO_4. Volume of test portion: 0.10 ml. Chart calibration: 1 inch of chart travel ≎ 0.0162 mequiv. Added to each test portion: 1.0 ml of 1.0 *M* NaF and 1.0 ml of 1.0 *M* $AlCl_3$

Test No.	*Chart travel inches*
1	5.63
2	5.65
3	5.60
4	5.70
5	5.60
Average	5.64

Relative standard error at 95% probability level = ±1.03%

The test solution was a solution of uranium tetrachloride originally estimated to contain 116 mg of uranium(IV) per ml. The uranium(IV) content gradually decreased because of air oxidation. At the time the test solution was analysed, the uranium(IV) content was estimated to be 108 mg/ml. No attempt was made to stabilize the solution. The precision data were obtained by making a series of titrations as quickly as possible in order to minimize the change in the uranium(IV) content.

Table III gives the results of a test run on an actual sample; the run was made for the purpose of establishing the bias. The sample was a solid derived from a fused-salt melt of zirconium fluoride and uranium fluoride. A 1.2958-g portion of this sample was dissolved by the use of aluminum chloride and sulfuric acid according to the procedure developed by ANONSEN AND FRENCH[7]. The resulting solution was diluted to a final volume of 50 ml with water. Aliquots were withdrawn from this final volume for titration. A plot of the data of Table III indicates the lack of bias in the method (Fig. 3).

TABLE III

RESULTS OF TITRATION OF URANIUM(IV) IN SAMPLE SOLUTION OF ZIRCONIUM FLUORIDE AND URANIUM FLUORIDE

Titrant: 1.0 N $K_2Cr_2O_7$. Diluent: 1.0 N H_2SO_4. Sample: ZrF_4-UF_4 dissolved in $AlCl_3-H_2SO_4$ solution[1]. Uranium (IV) content: 1.54 mg/ml. Chart calibration: 1 inch of chart travel ≎ 0.0162 mequiv.

Test No.	*Volume of test portion, ml*	*Chart travel inches*
1	1.00	0.80
2	2.00	1.65
3	3.00	2.45
4	4.00	3.20
5	5.00	4.35

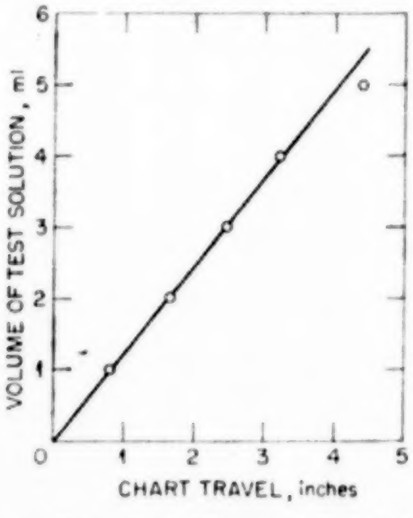

Fig. 3. Bias test (Data of Table III)

The applicability of the thermometric technique to the redox titration of a solution of uranium(IV) with a standard solution of potassium dichromate has been demonstrated. The thermometric technique offers an advantage over the potentiometric method in that the difficulties associated with the use of a noble-metal, indicator electrode are avoided[6].

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ACKNOWLEDGEMENT

Dr. M. T. Kelley gave us invaluable advice, and Mr. Harold C. Jones adapted the Greiner microburet to a constant-speed motor drive. We gratefully acknowledge their assistance.

SUMMARY

A thermometric method is presented for the redox titration of uranium(IV) with dichromate. The investigation was made primarily to determine the applicability of the thermometric method to redox titrations in solutions that contain ions deleterious to electrodes used in electrometric methods. A relative standard error of $\pm 1\%$ is attainable in the titration of quantities of uranium(IV) of the order of 5 mg. Less than 15 min is required to complete a titration. Fluoride ion can be tolerated in the solution provided that sufficient aluminum(III) is added to complex all the fluoride.

RÉSUMÉ

Une méthode thermométrique est proposée pour le titrage redox de l'uranium(IV) au moyen de dichromate. En présence d'ion fluorure, il est nécessaire d'ajouter de l'aluminium(III) en quantité suffisante pour le complexer totalement.

ZUSAMMENFASSUNG

Es wird eine thermometrische Methode zur Redox-Titration von Uran(IV) mit Dichromat beschrieben. Fluor-Ionen stören nicht, wenn sie durch Zugabe einer genügend grossen Menge von Aluminium(III) in die Komplexverbindung übergeführt werden.

REFERENCES

[1] P. Dutoit and E. Grobet, *J. chim. phys.*, 19 (1921) 324.
[2] R. H. Müller, *Ind. Eng. Chem., Anal. Ed.*, 13 (1941) 667.
[3] H. W. Linde, L. B. Rogers and D. N. Hume, *Anal. Chem.*, 25 (1953) 404.
[4] J. Jordan and T. G. Alleman, *Anal. Chem.*, 29 (1957) 9.
[5] I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.*, 55 (1933) 1971.
[6] I. M. Kolthoff and N. H. Furman, *Potentiometric Titrations*, 2nd Ed., John Wiley and Sons, New York, 1931.

[7] S. H. Anonsen and C. L. French, *A.E.C. Report NYO-5176*, March 1946 (Classified).

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THERMAL DECOMPOSITION OF SOME RARE EARTH METAL CUPFERRATES AND NEOCUPFERRATES

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Cupferron (ammonium salt of *N*-nitrosophenylhydroxylamine) and neocupferron (ammonium salt of *N*-nitrosonaphthylhydroxylamine) have been proposed as organic precipitants for the gravimetric determination of the lighter rare earth elements[1]. Previous thermobalance studies have shown that reagent is coprecipitated with the metal cupferrates, making it necessary to ignite and weigh as the metal oxides[2]. The metal neocupferrates required the same procedure[3].

As was anticipated, the heavier rare earth ions, those from europium to ytterbium, are also precipitated by these reagents. With the objective in mind that these two reagents may prove useful as analytical precipitants for the heavier rare earth metal ions, the metal cupferrates and neocupferrates were prepared and subjected to thermal decomposition on the thermobalance. Such information, as with the lighter rare earth metal chelates, is needed in order to determine the weighing form of the precipitates.

EXPERIMENTAL

Reagents

Cupferron and neocupferron were obtained from the Matheson, Coleman, and Bell Co., East Rutherford, N. J. They were used without further purification.

The rare earth samples were obtained as the oxides of 99.9% purity from Research Lab., Inc., Newtown, Ohio. The purity was that listed by the supplier.

All other reagents were of analytical reagent-grade quality.

Thermobalance

An automatic recording thermobalance which has previously been described was used[1]. The sample sizes ranged in weight from 60 to 90 mg and were run in duplicate or triplicate. A linear heating rate of 5.4° was used on all of the samples. During the pyrolysis of the samples, a slow stream of air was passed through the furnace to remove the decomposition products.

Preparation of chelates

The rare earth metal cupferrates and neocupferrates were prepared by the same general procedure as previously described[1]. The precipitates were air dried at room temperature for 24 h before being pyrolyzed on the thermobalance.

DISCUSSION

The thermograms of the rare earth metal cupferrates and neocupferrates are given in Figs. 1 and 2 with the composition data given in Table I.

Europium cupferrate

(Fig. 1F) The compound began to lose weight slowly beginning at 85°. At 150° the first break, but not a horizontal weight level, was found in the curve, followed by a very rapid weight loss above 170°. A second break in the curve was observed at 265° followed by further weight loss above 320°. An almost horizontal weight level was then found beginning at 415°, resulting in the formation of the oxide level, Eu_2O_3, at 570°.

TABLE I

COMPOSITION DATA FOR RARE EARTH CUPFERRATES AND NEOCUPFERRATES

Rare earth	*% Metal oxide*			
	Cupferrate		*Neocupferrate*	
	Theoretical	*Found*	*Theoretical*	*Found*
Europium	31.24	31.4 31.9	24.66	24.0 24.0
Terbium	32.78	32.8 32.6	25.94	25.2 25.3
Dysprosium	32.49	32.3 32.6	25.75	26.4 26.6
Holmium	32.78	29.6 29.6	26.00	24.9 24.9
Erbium	33.04	28.8 28.4	26.24	25.8 25.8
Ytterbium	32.71	33.4 33.1	26.82	24.8 24.8

Terbium cupferrate

(Fig. 1E) From the composition data, the air-dried chelate corresponded exactly to that expected for $TbCup_3$; where Cup is the cupferron ion. The first weight loss began at 85°, slowly at first, but becoming very rapid above 205°. A break in the curve was observed at 265° with further weight loss above 325°, resulting in the Tb_4O_7 level at 540°.

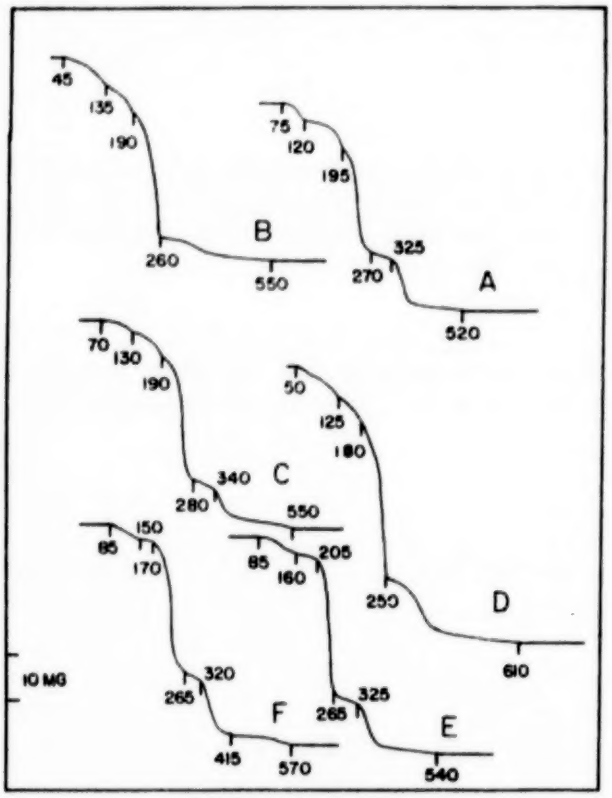

Fig. 1. Thermograms of the metal cupferrates. A. ytterbium, B. erbium, C. dysprosium, D. holmium, E. terbium, F. europium.

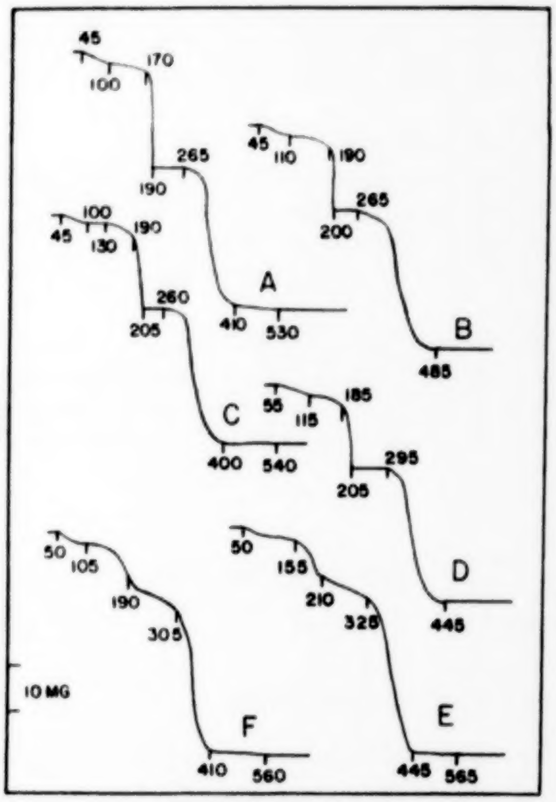

Fig. 2. Thermograms of the metal neocupferrates. A. erbium, B. ytterbium, C. dysprosium, D. holmium, E. terbium, F. europium.

Dysprosium cupferrate

(Fig. 1C) The composition of the chelate corresponded to the formula, $DyCup_3$, when air dried at room temperature. The first weight loss began at 70°, somewhat less than that found for $TbCup_3$. Breaks were observed in the curve at 130°, 190°, and 280°. The final oxidation of the organic matter began at about 340°, resulting in the Dy_2O_3 level at 550°.

Holmium cupferrate.

(Fig. 1D) This chelate began to lose weight at a low temperature, probably because of coprecipitated cupferron. The composition data shows a smaller percentage of oxide than the theoretical amount, indicating coprecipitation of reagent.

After the first weight loss at 50°, breaks in the curve were observed at 125°, 180°, and 250°. The final oxidation of the organic matter began at 250°, resulting in the Ho_2O_3 level at 610°.

Erbium cupferrate

(Fig. 1B) This chelate was the least stable of all of the metal cupferrates studied. Again, as in the case of $HoCup_3$, this was probably due to coprecipitated reagent. The first weight loss began at 45°, with breaks in the curve at 135°, 160°, and 260°. The Er_2O_3 level began at 550°.

Ytterbium cupferrate

(Fig. 1A) The first weight loss was observed at 75°, with breaks in the curve at 120°, 195°, and 270°. Final oxidation of the organic matter began at 325°, resulting in the Yb_2O_3 level at 520°.

Europium neocupferrate

(Fig. 2F) The composition of the air-dried metal chelate corresponded approximately to the formula, $Eu(Neocup)_3$; where Neocup is the neocupferron ion. The first weight loss was observed at 50°, with breaks in the curve at 105° and 190°. The initial weight loss did not correspond to the evolution of an entity of molecular weight 18 as was found in the lighter rare earth neocupferrates[3]. A horizontal weight level was not observed in the curve after this initial weight loss as was previously found. Beyond 305° the weight loss was quite rapid, resulting in the Eu_2O_3 level at 560°.

Terbium neocupferrate

(Fig. 2E) The composition of the air-dried chelate corresponded closely to the formula, $Tb(Neocup)_3$. The first weight loss began at 50°, slowly at first, but becoming quite rapid above 155°. A break in the curve was observed at 210°, with further rapid weight loss above 325°. The Tb_4O_7 level began at 565°.

Dysprosium neocupferrate

(Fig. 2C) The first weight loss began at 45° with a horizontal weight level being observed from 100° to 130°. The composition of the curve in this region is not known. Beyond 190° the chelate decomposed very rapidly, forming another horizontal weight level from 205° to 260°. This same general thermogram pattern is different from the previous two chelates but similar to the neocupferrates of Ho, Yb, and Er. Above 260° the chelate decomposed rapidly, resulting in the Dy_2O_3 level at 540°.

Holmium cupferrate

(Fig. 2D) The first weight loss began at 55° with a break in the curve, but not a horizontal weight level, at 115°. Beyond 185° the chelate decomposed rapidly, resulting in a horizontal weight level extending from 205 to 295°. The composition of the curve in this level is not known. Beyond 295° the organic matter began to oxidize rapidly, resulting in the Ho_2O_3 level at 445°.

Erbium neocupferrate

(Fig. 2A) The air-dried chelate began to lose weight at 45°. After a break in the curve at 100°, the weight loss was quite slow until 170°. Above this temperature, the chelate lost weight rapidly, giving a horizontal weight level from 190 to 265°.

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Beyond 265° the remaining organic matter oxidized rapidly, resulting in the Er_2O_3 level at 530°.

Ytterbium neocupferrate

(Fig. 2B) The first weight loss began at 45°, giving a break in the curve at 110°. Above this temperature the weight loss was slow until about 190°, where the weight loss became quite rapid. A horizontal weight level was then observed from 200 to 265° with additional rapid weight loss about 265°. The Yb_2O_3 level began at 485°.

General

In general, the heavier rare earth metal cupferrates and neocupferrates were less stable thermally than the corresponding lighter rare earth compounds. However, the minimum oxide level temperatures were in the same general temperature range.

The thermograms show that it is not possible to dry the precipitated complexes to constant weight and then weigh as the stoichiometric metal chelates. In several cases, the amount of metal oxide found for the metal chelates was less than the theoretical amount, indicating coprecipitation of the reagent. This phenomena was found even if a stoichiometrical amount of reagent was used to precipitate the rare earth metal ions.

The exact decomposition mechanism of the metal complexes is not known so it is difficult to assign definite compositions to all parts of the thermal decomposition curve. However, from the first weight loss temperature to the minimum oxide level temperature, the curve probably represents the resultant of a mixture of two or more different compounds. It appears fairly certain that the metal complexes are not hydrated so that the first weight losses are not due to the loss of hydrate-bound water.

SUMMARY

The thermal decomposition of the cupferrates and neocupferrates of europium, terbium, dysprosium, holmium, erbium, and ytterbium was studied on the thermobalance. The metal chelates possessed poor thermal stability as well as a pronounced tendency to coprecipitate reagent. The minimum oxide level temperatures for the metal cupferrates were: Eu, 570°; Tb, 540°; Dy, 550°; Ho, 610°; Er, 550°; and Yb, 520°. The minimum oxide level temperatures for the metal neocupferrates were: Eu, 560°; Tb, 565°; Dy, 540°; Ho, 445°; Er, 530°; and Yb, 485°.

RÉSUMÉ

On a examiné la décomposition thermique des cupferrates et néocupferrates d'europium, de terbium, de dysprosium, d'holmium, d'erbium et d'ytterbium sur la thermobalance. Ces composés présentent une faible stabilité thermique.

ZUSAMMENFASSUNG

Es wurde die thermische Zersetzung der Kupferron-undNeokupferron-Komplexe von Europium, Terbium, Dysprosium, Holmium, Erbium und Ytterbium auf der Thermowage untersucht. Diese Verbindungen besitzen nur eine geringe Wärmestabilität.

REFERENCES

[1] A. I. Popov and W. W. Wendlandt, *Anal. Chem.*, 26 (1954) 883.
[2] W. W. Wendlandt, *Anal. Chem.*, 27 (1955) 1277.
[3] W. W. Wendlandt and J. M. Bryant, *Anal. Chim. Acta*, 13 (1955) 550.
[4] W. W. Wendlandt, *Anal. Chem.*, 30 (1958) 56.

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DETERMINATION OF NIOBIUM AND TANTALUM IN BINARY ALLOYS AND ZIRCONIUM ALLOYS

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INTRODUCTION

Preparation of zirconium alloys containing substantial amounts of niobium and tantalum, which have been proposed for use in nuclear reactors, and the development of niobium-tantalum alloys for evaluation of their properties, especially at elevated temperatures, created a need for rapid methods of determining niobium and tantalum in the presence of each other and in zirconium.

Provision of such methods is made more difficult because of the chemical similarity of these elements and the marked influence which they exercise on the normal reactions of each other in solution.

Published methods are intended principally for the examination of ores and minerals, and usually involve separation of niobium and tantalum from each other and from associated elements. Separation of niobium and tantalum from other elements has been achieved by chemical methods, *e.g.* selective precipitation of their fluorides, acids or tannin complexes[1], and by physical methods, *e.g.* fractional distillation of their volatile chlorides[2]. These procedures, however, are time-consuming and separations are often incomplete, especially in the presence of large amounts of zirconium (or titanium). More recently, chromatographic methods have been described[3,4], in which niobium and tantalum are extracted from a fluoride solution on a cellulose column, with ethyl methyl ketone containing dilute hydrofluoric acid. In this way, niobium and tantalum can be separated from the majority of metals. Other methods for separating niobium, tantalum, zirconium and titanium from one another are based on selective extraction from acid solution, by means of organic solvents such as isobutyl methyl ketone, di-isobutyl ketone or cyclohexanone[5-7]. After separation by any of these methods, niobium and tantalum are usually separately determined either by gravimetric or absorptiometric procedures.

Absorptiometric methods have been described for determining niobium and tantalum in ores[1] without recourse to a preliminary separation, unless significant amounts of interfering elements are present. Niobium has been determined by procedures based on the yellow colour formed when a solution of the metal reacts with thiocyanate ions in hydrochloric–tartaric acid solution containing acetone as a colour stabiliser[8,9], but in our experiments zirconium caused serious interference. A procedure depending on the formation of a yellow niobium–peroxide complex in sulphuric–phosphoric acid solution[10], has also been described, but the reaction is not very sensitive. A colorimetric procedure, based on the formation of a tantalum–

catechol complex in hydrochloric–sulphuric–oxalic acid solution, has been described[11] for the determination of tantalum.

Both niobium and tantalum form soluble, yellow complexes with pyrogallol in ammonium oxalate solution[12,13]. Tantalum is determined in acid pyrogallol solution and under these conditions, interference by niobium is small, but in alkaline pyrogallol solution the order of sensitivity is reversed.

All these colorimetric procedures are subject to interference by other metals, such as iron, molybdenum, tungsten and particularly titanium; where the effect is small a correction can often be applied, but significant amounts of these metals must be separated.

In order to provide methods for determining niobium and tantalum in their binary alloys and in zirconium, the pyrogallol reaction, because of its direct application to both niobium and tantalum, was selected for investigation.

EXPERIMENTAL

I. DETERMINATION OF NIOBIUM IN TANTALUM AND ZIRCONIUM

Preliminary experiments

Initial experiments were made (a) to determine the most suitable wavelength at which to measure absorption of the niobium–pyrogallol complex in the presence of tantalum and zirconium complexes; and (b) using this wavelength, to prepare a calibration graph. The concentrations of reagents used in this preliminary work were accurately controlled as recommended by HUNT AND WELLS[13].

(*a*) *Absorption curves.* High purity niobium pentoxide (71.5 mg) was fused with 10 g of potassium bisulphate in a small platinum dish, and the cooled melt was extracted with about 200 ml of hot water containing 20 g of ammonium oxalate. The solution was diluted to 500 ml in a calibrated flask; then:

1 ml ≡ 0.1 mg of niobium.

To 2.5 ml of this solution, contained in a 50-ml calibrated flask, 17.5 ml of ammonium oxalate solution (4%) were added, followed by 4.5 ml of potassium bisulphate solution (10%), thus bringing the total amounts of these reagents in solution to 0.8 g and 0.5 g respectively. 20 ml of pyrogallol reagent (2.0% in 20% sodium sulphite solution) were added, the solution was diluted to the mark, then set aside for 15 min at 20°. O. D. measurements were made at wavelengths between 3600 Å and 4800 Å, using a Unicam S.P. 600 spectrophotometer and 2-cm cells.

Further absorption curves were prepared as described above, using:

(1) reagents only, in order to ascertain blank values at various wavelengths;

(2) 2.5 ml of tantalum solution
(1 ml ≡ 0.3 mg of tantalum);

(3) 7.5 ml of zirconium solution
(1 ml ≡ 1.0 mg of zirconium).

None of the curves (Fig. 1) showed a peak of maximum absorption, and in every instance absorption decreased with increase in wavelength; the absorption/mg of metal was greatest for niobium and least for zirconium. The absorption-ratio curve of the niobium and tantalum complexes at various wavelengths (Fig. 2) approached a maximum at about 4500 Å, and this was also true for the absorption-ratio curve of the niobium and zirconium complexes. A wavelength of 4500 Å was therefore selected for preparation of calibration and correction graphs. At 4500 Å, absorption by the niobium complex was only about half that at 4100 Å, the wavelength recommended by HUNT AND WELLS[13], but absorption by the tantalum or zirconium complexes at 4500 Å was about one fifth of that obtained at the lower wavelength.

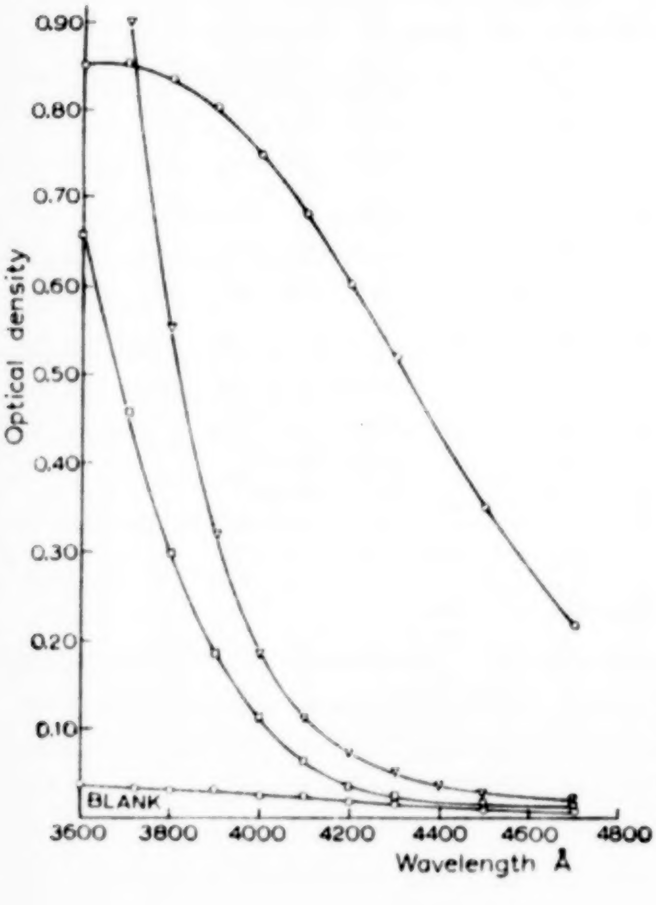

Fig. 1. Absorption curves of niobium, tantalum and zirconium/pyrogallol complexes and "blank" solution (alkaline medium). Niobium ○ 0.25 mg/50 ml; tantalum □ 0.75 mg/50 ml; zirconium ▽ 7.5 mg/50 ml; cell 2 cm.

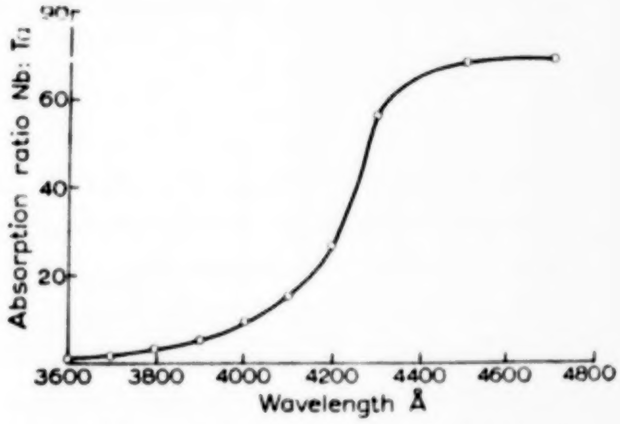

Fig. 2. Absorption ratio curve of niobium to tantalum pyrogallol complexes at various wavelengths. Niobium 0.25 mg/50 ml; tantalum 0.75 mg/50 ml; cell 2 cm.

(*b*) *Calibration and correction graphs.* Volumes of niobium solution (1 ml ≡ 0.1 mg of niobium) up to 5.0 ml were transferred to 50-ml calibrated flasks and reagents were added in accordance with the procedure outlined in (a), the weight of ammonium oxalate and potassium bisulphate being adjusted, as before, to 0.8 g and 0.5 g respectively. These solutions were diluted to the mark and optical densities were determined at 4500 Å, using 2-cm cells; a linear calibration graph was obtained. A differential calibration graph was also prepared, using solutions containing 1.0 to 1.4 mg of niobium/50 ml measured against a solution containing 1.0 mg of niobium/50 ml.

Correction graphs to compensate for tantalum and zirconium were prepared at 4500 Å by the procedure described in (b), using solutions containing tantalum up to 20 mg, and solutions containing similar amounts of zirconium; both graphs were linear.

Niobium was then determined in solutions containing major amounts of tantalum. These solutions were prepared by fusing a mixture of the metals in potassium bisulphate and extracting the cooled melts with ammonium oxalate solution. Aliquots were transferred to 50-ml calibrated flasks and treated as described previously; after correcting for absorption due to tantalum, satisfactory results were obtained. Similar determinations were made using solutions containing major amounts of zirconium. Results of these tests are shown in Table I, Test Nos. 1, 2, 6 and 7.

TABLE I

DETERMINATION OF NIOBIUM IN THE PRESENCE OF ZIRCONIUM OR TANTALUM

Test No.	*Zirconium + Niobium (g)*	*Niobium %*	
		Present	*Determined*
1	0.15	2.1	2.07 2.05
2	0.10	5.1	5.07 4.98
3	0.125	10.7	10.57 10.64
4	0.075	14.7	14.72 14.60 14.72 14.72 14.62
5	0.06	20.7	20.70 20.49
	Tantalum + Niobium (g)		
6	0.15	2.1	1.96 2.0
7	0.10	5.2	5.19 5.20
8	0.125	10.0	9.89 10.06
9	0.06	20.7	20.87 20.92

Effects of temperature and concentration of reagents

Tests showed that the O. D. of the niobium complex decreased over the range 10 to 30° by 0.007 per degree C rise. In subsequent tests, therefore, solution temperatures were controlled at 20° ± 1° during O. D. measurements. Variation in blank values, over the same temperature range, was negligible. Full development of colour was obtained within 5 min after diluting the solution to the calibration mark, and the colour was stable for at least 90 min. Blank values also remained constant over the same period.

With increase in the amount of alkaline pyrogallol solution (2%), over the range 5 to 15 ml, O. D. increased rapidly, but thereafter, up to 25 ml, the increase in O. D.

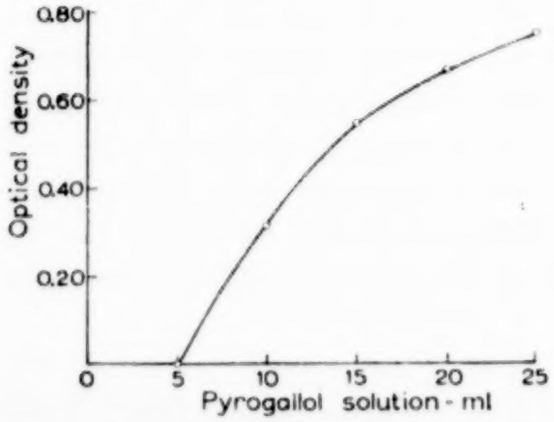

Fig. 3. Effect of alkaline pyrogallol (2%). Niobium 0.5 mg/50 ml; wavelength 4500 Å; cell 2 cm.

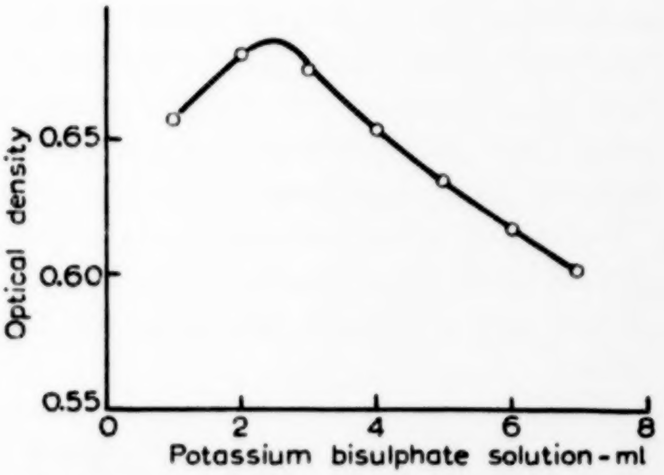

Fig. 4. Effect of potassium bisulphate (10%). Niobium 0.5 mg/50 ml; wavelength 4500 Å; cell 2 cm.

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was more gradual. Below 5 ml, the coloured complex was not formed (Fig. 3). The amount of reagent added in subsequent experiments was therefore controlled at 20 ml ± 0.05 ml.

Over the range 1 to 2.5 ml, increase in the amount of potassium bisulphate solution (10%) caused an increase in optical density, but from 2.5 to 7 ml the O. D. decreased (Fig. 4). The amount of solid reagent used for dissolution of the sample must be weighed to within ± 50 mg.

Increase in the amount of ammonium oxalate solution (4%) from 5 to 25 ml caused a linear decrease in O. D. and the amount of this reagent, used to prevent hydrolysis, must be weighed to within ± 50 mg.

Effect of other metals

In common with many other phenolic compounds, pyrogallol forms coloured complexes with numerous ions. Tests to determine the effects of common alloying constituents and likely impurities showed that, under the conditions used for determining niobium by the recommended method, coloured complexes were formed by copper, iron, molybdenum, tungsten and titanium, in addition to tantalum and zirconium. The extent of interference by these metals is shown in Table II.

TABLE II

EFFECT OF OTHER METALS IN THE DETERMINATION OF NIOBIUM

Metal (*1 mg*)	*Niobium equivalent* (*mg*)
Copper	<0.001
Tin	<0.001
Iron	1.34
Molybdenum	1.20
Tungsten	0.02
Titanium	2.97
Tantalum	0.003
Zirconium	0.001

Interference by tantalum and zirconium was small, and a suitable compensation can be made by using correction graphs, as described earlier. A correction for iron up to about 0.3% can be made, by determining the iron content of the sample (using thioglycollic acid) and deducting four thirds of the value obtained from the apparent niobium content of the sample. Amounts below about 5% of copper or tin, or 1% of tungsten, had a negligible effect. Interference by molybdenum became significant above about 0.02% but this metal can be separated, as described in the method. Titanium above about 0.01% caused serious interference.

Application of the method

Because of the corrections to be applied in the presence of tantalum, zirconium and possible impurities, the procedure is limited to amounts of niobium above about 2%. The calibration graph is, therefore, applicable over the range 2 to 3%, based on a 0.15-g sample, but the method has been extended to the determination of up to about 7% of niobium by using a proportionally smaller sample weight. Experiments have shown (Table I, Test Nos. 3, 4, 5, 8 and 9) that up to about 20% of niobium can be satisfactorily determined by the recommended differential procedure.

The method was applied to samples of niobium–zirconium alloys containing from 5 to 20% of niobium, and satisfactory results were obtained (Table III).

TABLE III

DETERMINATION OF NIOBIUM IN ZIRCONIUM–NIOBIUM ALLOYS

Sample No.	*Niobium %*			
	Nominal	*Determined*		
1	5.0	5.10	5.14	5.07
2	15.0	14.90	14.83	
3	20.0	19.72	19.77	
4 (Zirconium/6.5% Sn/10% Nb)	10.0	8.93	8.99	
		8.96[a]	8.92[a]	

[a] Tin removed by a preliminary sulphide precipitation

2. DETERMINATION OF TANTALUM IN NIOBIUM AND ZIRCONIUM

Preliminary experiments

Initial tests were made (a) to establish the most suitable wavelength at which to measure absorption of the tantalum–pyrogallol complex in the presence of niobium and zirconium complexes, and (b) using this wavelength, to prepare a calibration graph.

(*a*) *Absorption curves.* High purity tantalum pentoxide (0.1221 g) was fused with 10 g of potassium bisulphate in a small platinum dish, and the cooled melt was extracted with about 200 ml of hot water containing 20 g of ammonium oxalate. The solution was diluted to 500 ml in a calibrated flask. Then:

$$1 \text{ ml} \equiv 0.2 \text{ mg of tantalum.}$$

To 7.5 ml of this solution, contained in a 50-ml calibrated flask, 17.5 ml of ammonium oxalate solution (4%) were added, followed by 3.5 ml of potassium bisulphate solution (10%); the total amounts of these reagents in solution were 1.0 and 0.5 g respectively. 5 ml of pyrogallol reagent (15.0% in sulphuric acid (1 + 40)) were added, the solution was diluted to the mark, and set aside for 15 min at 20°. Optical density measurements were made at wavelengths between 3600 Å and 4800 Å, using a Unicam S.P. 600 spectrophotometer and 2-cm cells. The wavelength of maximum absorption of the tantalum complex was found to be at 4000 Å (Fig. 5).

Further absorption curves were prepared as described above, using:

(1) reagents only

(2) 20 ml of niobium solution (1 ml ≡ 1.0 mg of niobium).

Absorption by the niobium complex and the blank were small, and both decreased with increase in wavelength (Fig. 5). The small absorption by the niobium complex at 4000 Å indicated that a correction graph could be used to compensate for amounts of niobium up to about 20 mg.

Further tests showed that solutions containing up to 20 mg of zirconium/50 ml had negligible absorption at 4000 Å under the conditions described above.

(b) Calibration and correction graphs. Amounts of tantalum solution (1 ml ≡ 0.2 mg of tantalum) ranging from 0 to 7.5 ml were transferred to 50-ml calibrated flasks, and reagents were added in accordance with the procedure described in (a), the weights of ammonium oxalate and potassium bisulphate being adjusted as before to 1.0 g and 0.5 g respectively. These solutions were diluted to the mark and optical densities were determined at 4000 Å, using 2-cm cells; a linear calibration graph was obtained. A differential calibration graph was also prepared using solutions containing 1.5 to 3.0 mg of tantalum/50 ml measured against a solution containing 1.5 mg of tantalum/50 ml.

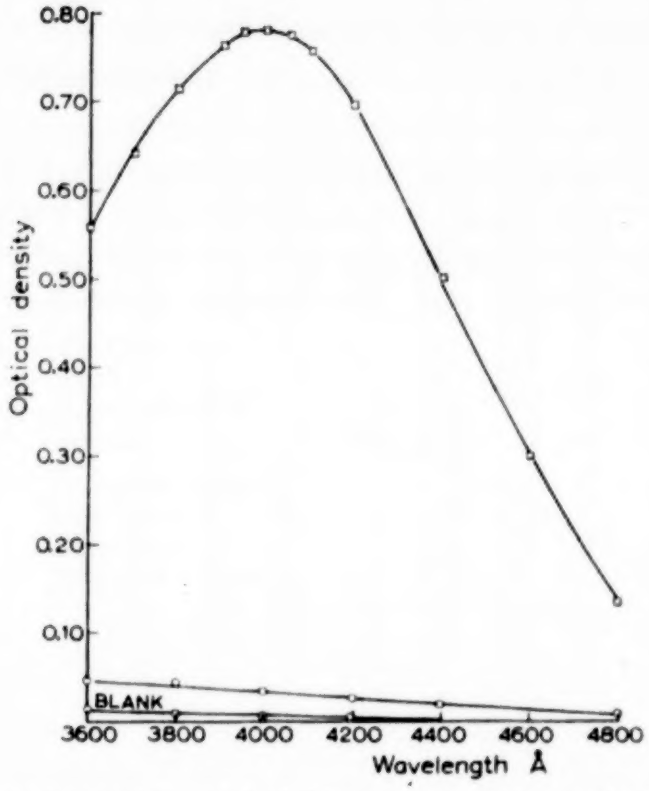

Fig. 5. Absorption curves of tantalum and niobium pyrogallol complexes and "blank" solution (acid medium). Tantalum □ 1.5 mg/50 ml; niobium ○ 20.0 mg/50 ml; cell 2 cm.

A correction graph for niobium was prepared at 4000 Å by the procedure described in (b), using solutions containing niobium up to 25 mg; the graph obtained was linear.

TABLE IV

DETERMINATION OF TANTALUM IN THE PRESENCE OF ZIRCONIUM OR NIOBIUM

Test No.	*Zirconium + Tantalum* (g)	*Tantalum %* *Present*	*Determined*
1	0.15	2.0	1.96 1.95
2	0.25	10.0	10.00 10.00
3	0.15	15.0	15.00 15.00
	Niobium + Tantalum (g)		
4	0.15	5.0	4.95 4.95
5	0.25	10.0	9.95 9.88
6	0.15	14.8	14.80 15.00
7	0.15	20.0	19.92

Tantalum was then determined in solutions containing major amounts of niobium and, after correcting for absorption due to niobium, satisfactory results were obtained. Similar tests, in the presence of major amounts of zirconium, also gave satisfactory results (Table IV, Test Nos. 1 and 4).

Effects of temperature and concentration of reagents

The optical density of the tantalum complex decreased over the range 10 to 30° by 0.0085 per degree C rise. In subsequent tests, therefore, solution temperatures were controlled at 20° ± 1° during optical density measurements. Variation in blank values over the same temperature range, was negligible. Full development of colour was obtained within 5 min after diluting the solution to the calibration mark, and the colour was stable for at least 90 min. Blank values also remained constant over the same period.

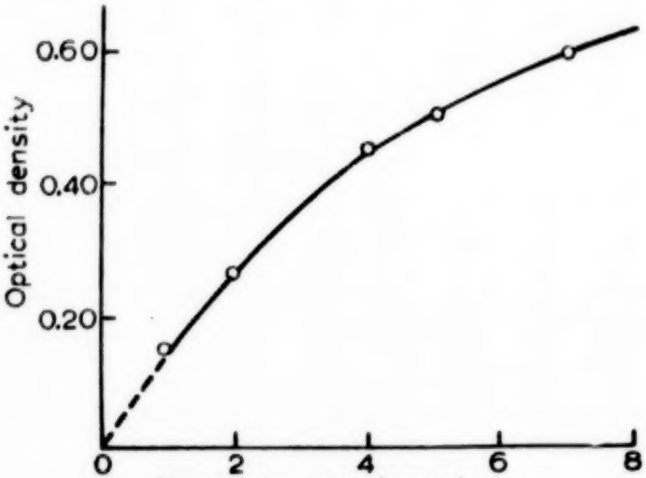

Fig. 6. Effect of acid pyrogallol (15%). Tantalum 1.0 mg/50 ml; wavelength 4000 Å; cell 2 cm.

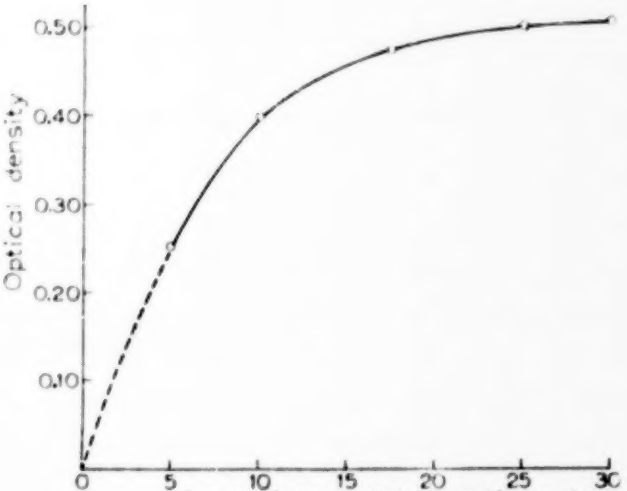

Fig. 7. Effect of ammonium oxalate (4%). Tantalum 1.0 mg/50 ml; wavelength 4000 Å; cell 2 cm.

With increase in the amount of acid pyrogallol solution (15%), up to 7 ml (Fig. 6) there was an increase in the optical density of the complex. The amount of reagent added in subsequent tests was controlled at 5 ml ± 0.05 ml.

Over the range 1 to 9 ml, increase in the amount of potassium bisulphate (10%) caused a linear increase in optical density. The amount of solid reagent used for dissolution of the sample must be weighed to within ± 50 mg.

Increase in the amount of ammonium oxalate solution (4%) from 2 to 10 ml caused a sharp increase in optical density; from 10 to 30 ml the increase was more gradual, (Fig. 7). The amount used, to prevent hydrolysis, must be weighed to within ± 50 mg.

Effects of other metals

Tests to determine the effects of common alloying constituents and likely impurities showed that, under the conditions for determining tantalum by the recommended method, coloured complexes were formed by copper, iron, molybdenum, tungsten and titanium, in addition to niobium. The extent of interference by these metals is shown in Table V. No interference was caused by zirconium up to at least 98%. Interference by niobium was small and a suitable compensation can be made using a correction graph, as described earlier. A correction for iron, up to about 1.0% can be made by determining the iron content of the sample, using thioglycollic acid, and subtracting one fifth of the value obtained from the apparent tantalum content of the sample. Amounts up to about 5% of copper, aluminium or nickel, or 0.2% of tungsten had no significant effect. Interference by molybdenum became significant above about 0.05%, but this metal can be separated, as described in the method. Titanium above about 0.01% caused serious interference.

TABLE V

EFFECTS OF OTHER METALS IN THE DETERMINATION OF TANTALUM

Metal (1 mg)	*Tantalum equivalent (mg)*
Copper	0.004
Iron	0.18
Aluminium	<0.001
Nickel	0.003
Molybdenum	0.33
Tungsten	0.08
Titanium	3.84
Niobium	0.004

Application of the method

Determination of tantalum by the direct procedure is limited to amounts above about 2%, and the useful range of the calibration graph is from about 2 to 7%, based on a 0.15-g sample. Tests have shown (Table IV, Test Nos. 2, 3, 5 to 7) that amounts up to about 20% of tantalum can be satisfactorily determined by the recommended differential procedure.

The method was applied to samples of niobium–tantalum alloys containing 15 to 30% of tantalum, and satisfactory results were obtained (Table VI).

TABLE VI

DETERMINATION OF TANTALUM IN ZIRCONIUM–TANTALUM AND NIOBIUM–TANTALUM ALLOYS

Sample No.	*Tantalum %*	
	Nominal	*Determined*
1 (Niobium/15%Ta/5%Mo alloy)	15.0	15.20 15.05
2 (Niobium/15%Ta/5%Mo alloy)	15.0	15.1 15.3
3 Zirconium/Ta alloy	27–28	27.9 27.9 28.0 28.0.

METHODS

1. DETERMINATION OF NIOBIUM IN ZIRCONIUM AND TANTALUM

Special reagents

Ammonium oxalate solution (4%). Dissolve 40.0 g of $(NH_4)_2C_2O_4 \cdot H_2O$ in about 900 ml of warm water, cool and dilute to 1 l.

Potassium bisulphate solution (10%).

Sodium sulphite solution (20%). Dissolve 50 g of $Na_2SO_3 \cdot 7\ H_2O$ in about 150 ml of water and dilute to 250 ml. Prepare this solution immediately before use.

Alkaline pyrogallol solution (2.0%). Dissolve 2.0 g of pyrogallol in about 40 ml of sodium sulphite solution (20%), then filter through a No. 40 Whatman paper into a dry, 100-ml calibrated flask. Wash the paper with sufficient sodium sulphite solution to dilute the filtrate to 100 ml.

Standard niobium solution. Calcine about 0.1 g of high-purity niobium pentoxide at 850°, for 30 min. Cool, transfer 71.5 mg of the calcined oxide to a small platinum dish and fuse with 10.0 g of potassium bisulphate. Cool, transfer the dish and contents to a beaker (400 ml) and extract with a hot solution of 20.0 g of ammonium oxalate in about 250 ml of water. Heat gently until the melt has dissolved, then transfer the cooled solution to a 500-ml calibrated flask and dilute to the mark.

1 ml ≡ 0.1 mg of niobium.

Standard zirconium solution. Fuse 80 mg of iodide-zirconium with 2.0 g of potassium bisulphate in a conical flask (100 ml). Cool, extract with a hot solution of 3.2 g of ammonium oxalate in about 60 ml of water. Heat gently until the melt has dissolved, then transfer the cooled solution to a 100-ml calibrated flask and dilute to the mark.

1 ml ≡ 0.8 mg of zirconium

Standard tantalum solution. Fuse 0.122 g of high purity tantalum pentoxide with 2.0 g of potassium bisulphate in a conical flask (100 ml). Cool, extract with a hot solution of 4.0 g of ammonium oxalate in about 60 ml of water and continue as described for preparation of the zirconium solution, then:

1 ml ≡ 1.0 mg of tantalum.

Preparation of calibration graphs

Graph 1. For niobium content 2–7%. Add, separately, 1.0, 2.0, 3.0, 4.0 and 5.0 ml of the standard niobium solution (1 ml ≡ 0.1 mg Nb) to five 50-ml calibrated flasks. Add to each, and a blank, sufficient ammonium oxalate solution (4%) and potassium bisulphate solution (10%) to bring the volumes of these reagents to 20.0 ml and 5.0 ml respectively. Thus:

Standard niobium solution, ml	*Ammonium oxalate solution, ml*	*Potassium bisulphate solution, ml*
1.0	19.0	4.8
2.0	18.0	4.6
3.0	17.0	4.4
4.0	16.0	4.2
5.0	15.0	4.0
NIL	20.0	5.0

Add to each, 20.0 ml of alkaline pyrogallol solution (2%), dilute to the mark and allow to stand for 15 min at 20° ± 1°. Measure the optical densities at a wavelength of 4500 Å, using 2-cm cells.

Graph 2. For niobium content 7–20%. Prepare these solutions simultaneously with the sample solution(s).

Add, separately, 10.0, 11.0, 12.0, 13.0 and 14.0 ml of the standard niobium solution (1 ml ≡ 0.1 mg Nb) to five 50-ml calibrated flasks. Add ammonium oxalate solution (4%) and potassium bisulphate solution (10%) to bring the total volume of these reagents to 20.0 ml and 5.0 ml respectively. Add 20.0 ml of the alkaline pyrogallol solution (2%), dilute to the mark and allow to stand for 15 min at 20° ± 1°. Use these solutions at the appropriate stage in the differential procedure 2.

Preparation of correction graphs

(*a*) *For zirconium.* Add, separately, 5.0, 12.5, 17.5, and 25.0 ml of the standard zirconium solution (1 ml $\equiv$ 0.8 mg Zr) to four 50-ml calibrated flasks, and continue as described for preparation of calibration Graph 1.

(*b*) *For tantalum.* Add, separately, 5.0, 10.0, 15.0 and 20.0 ml of the standard tantalum solution (1 ml $\equiv$ 1.0 mg Ta) to four 50-ml calibrated flasks and continue as described in (a).

Procedure 1. For niobium content 2–7%. Make a reagent blank determination and check at least two points on the calibration graph with each batch of samples.

Transfer a suitable weight of sample (Note 1) to a dry conical flask (100 ml), add 5.0 g of potassium bisulphate and heat over a Bunsen flame until the sample has dissolved (Note 2). Cool, extract, with a hot solution of 8.0 g of ammonium oxalate in about 60 ml of water; heat gently until the melt has dissolved. Cool (crystals will separate at this stage) and wash the solution into a 250-ml calibrated flask; shake to dissolve any crystals and dilute to the mark. Transfer a 25-ml aliquot to a 50-ml calibrated flask, add 20.0 ml of alkaline pyrogallol solution (2.0%) and dilute to the mark. Allow to stand for 15 min at 20° ± 1° and measure the optical density at 4500 Å, using 2-cm cells. Correct for absorption due to zirconium and/or tantalum and calculate the niobium content of the sample, using the calibration graph.

Procedure 2. For niobium content 7–20%. Transfer a suitable weight of sample (*Note 3*) to a dry conical flask (100 ml), add 5.0 g of potassium bisulphate and prepare the solutions for optical density measurement, as described in Procedure 1.

Rinse out two 2-cm cells marked "reference" and "test", once with water, twice with ethyl alcohol then once with ether. Allow the cells to drain, then polish the exterior surfaces with chamois leather.

To determine the cell blank, fill both cells with the 10.0-ml "reference" solution prepared for Graph 2, and measure the optical density with respect to each other at a wavelength of 4500 Å. Correct for this cell blank in all subsequent optical density measurements. Fill the "test" cell successively with the remaining calibration solutions, then with the sample solution(s). In each instance, determine the O. D. against the 10.0-ml "reference" solution. Prepare a graph relating O. D. to mg niobium/50 ml, correct for absorption due to zirconium and/or tantalum in the sample, and calculate the niobium content.

A calibration graph must be prepared with each batch of samples.

Notes

1. In order to facilitate fusion, the sample must be finely divided.

Suitable sample weights are as follows:

Nb(%)	*Sample weight (g)*
2–3	0.15
4–6	0.10
6–7	0.07

For samples which are difficult to dissolve in bisulphate proceed as follows:

Transfer the sample to a small platinum dish, add 10 ml of water and 1 ml of conc. nitric acid ($d = 1.42$) then heat gently and add hydrofluoric acid, dropwise. Evaporate the solution to

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dryness, calcine at 800° for about 10 min, fuse the oxides with 5.0 g of potassium bisulphate, then follow the recommended procedure.

2. To correct for the effect of iron, up to about 0.3%, determine the iron content of the sample, using thioglycollic acid, and deduct four thirds of the value obtained, from the apparent niobium content.

Molybdenum, above about 0.02%, interferes, but can be separated as follows:

Fuse the sample in potassium bisulphate and digest the cold melt with hot water for about 15 min. Cool, add 30 ml of ammonium hydroxide ($d = 0.925$), heat to boiling and maintain just below the boiling point for 15 min .Filter through a paper pulp pad, wash with a hot solution of ammonium hydroxide (1 + 50) containing about 5 g of ammonium nitrate/100 ml. Dry, char and finally calcine the precipitate at 800°. Fuse the oxides with 5.0 g of potassium bisulphate and continue as described in the procedure.

3. Suitable sample weights are as follows:

Nb(%)	*Sample weight (g)*
7–9	0.15
10–11	0.125
12–14	0.10
15–18	0.075
20	0.060

2. DETERMINATION OF TANTALUM IN ZIRCONIUM AND NIOBIUM

Special reagents

Acid pyrogallol solution (15%). Dissolve 15.0 g of pyrogallol in about 60 ml of water and 5.0 ml of sulphuric acid (1 + 1). Transfer the solution to a 100-ml calibrated flask and dilute to the mark. Filter through a No. 40 Whatman paper before use.

Standard tantalum solution. Calcine about 0.15 g of high-purity tantalum pentoxide at 850° for 30 min. Cool, transfer 0.1221 g of the calcined oxide to a small platinum dish and fuse with 10.0 g of potassium bisulphate. Cool, transfer the dish and contents to a beaker (400 ml) and extract with a hot solution of 20.0 g of ammonium oxalate in about 250 ml of water. Heat gently until the melt has dissolved, then transfer the cooled solution to a 500-ml calibrated flask and dilute to the mark.

1 ml = 0.2 mg of tantalum.

Standard niobium solution. Fuse 0.143 g of high-purity niobium pentoxide with 2.0 g of potassium bisulphate in a conical flask (100 ml). Cool, extract with a hot solution of 4.0 g of ammonium oxalate in about 60 ml of water. Heat gently until the melt has dissolved, then transfer to a 100 ml calibrated flask and dilute to the mark.

1 ml = 1.0 mg of niobium.

Preparation of calibration graphs

Graph 1. For tantalum content 2–7%. Add, separately, 2.0, 4.0, 6.0 and 7.5 ml of the standard tantalum solution (1 ml = 0.2 mg Ta) to four 50-ml calibrated flasks. Add to each, and a blank, sufficient ammonium oxalate solution (4%) and potassium bisulphate solution (10%) to bring the volumes of these reagents to 25.0 ml and 5.0 ml respectively. Thus:

Standard tantalum solution, ml	*Ammonium oxalate solution, ml*	*Potassium bisulphate solution, ml*
2.0	23.0	4.6
4.0	21.0	4.2
6.0	19.0	3.8
7.5	17.5	3.5
NIL	25.0	5.0

Add to each, 5.0 ml of the acid pyrogallol solution (15%), dilute to the calibration mark and allow to stand for 15 min at 20° ± 1°. Measure the optical densities at a wavelength of 4000 Å, using 2-cm cells.

Graph 2. For tantalum content 7–20%. Prepare these solutions simultaneously with the sample solution(s).

Add, separately, 7.5, 10.0, 12.5 and 15.0 ml of the standard tantalum solution (1 ml = 0.2 mg Ta) to four 50-ml calibrated flasks. Add ammonium oxalate solution (4%) and potassium bisulphate solution (10%) to bring the total volumes of these reagents to 25.0 ml and 5.0 ml respectively. Add 5.0 ml of the acid pyrogallol solution (15%), dilute to the mark and allow to stand for 15 min at 20° ± 1°. Use these solutions at the appropriate stage in the differential procedure 2.

Preparation of correction graph for niobium

Add, separately, 5.0, 12.5, 17.5 and 25.0 ml of the standard niobium solution (1 ml = 1.0 mg Nb) to four 50 ml calibrated flasks and continue as described for preparation of calibration Graph 1.

Procedure 1. For tantalum content 2–7%. Make a reagent blank determination and check at least two points on the calibration graph with each batch of samples.

Transfer 0.15 g of the sample to a dry conical flask (100 ml), add 5.0 g of potassium bisulphate and heat over a Bunsen flame until the sample has dissolved (Note 1). Cool, extract with a hot solution of 10.0 g of ammonium oxalate in about 60 ml of water; heat gently until the melt has dissolved. Cool, transfer the solution to a 250-ml calibrated flask and dilute to the mark. Transfer a 25-ml aliquot to a 50-ml calibrated flask, add 5.0 ml of acid pyrogallol solution (15%) and dilute to the mark. Allow to stand for 15 min at 20° ± 1° and measure the O. D. at 4000 Å, using 2-cm cells. If niobium is present, correct for absorption due to the niobium-pyrogallol complex and calculate the tantalum content of the sample, using the calibration graph.

Procedure 2. For tantalum content 7–20%. Transfer 0.15 g of the sample (Note 2) to a dry conical flask (100 ml), add 5.0 g of potassium bisulphate and prepare the solutions for O. D. measurement, as described in Procedure 1.

Prepare two 2-cm cells marked "reference" and "test" as described for the differential absorptiometric determination of niobium. To determine the cell blank, fill both cells with the 7.5-ml tantalum "reference" solution prepared for Graph 2 and measure the O. D. with respect to each other at a wavelength of 4000 Å. Correct for the cell blank in all subsequent O. D. measurements.

Fill the "test" cell successively with the remaining calibration solutions and finally with the sample solution(s). In each instance, determine the O. D. against the 7.5-ml "reference" solution. Prepare a calibration graph relating O. D. to mg tantalum/50 ml, correct for absorption due to niobium in the sample and calculate the tantalum content.

A calibration graph should be prepared with each batch of samples.

Notes

1. The sample must be finely divided. For samples which are difficult to dissolve, use the procedure described in Note 1, p. 131, for the *Determination of niobium in zirconium and tantalum.*

2. For samples containing 7–10% of tantalum, use 0.25 g of sample, dissolve as described in Note 1, p. 131.

To correct for the effect of iron, up to about 1.0%, determine the iron content of the sample, using thioglycollic acid and deduct one fifth of the value obtained from the apparent tantalum content. Molybdenum above about 0.05% interferes but can be separated as described in Note 2, p. 132.

CONCLUSIONS

The direct absorptiometric procedure using alkaline pyrogallol solution is suitable for determining niobium over the range 2 to 7% in zirconium and tantalum. The method can be extended to the determination of larger amounts of niobium, by using a differential procedure. Corrections must be applied for zirconium, tantalum or impurity amounts of iron. Amounts up to 5% of copper or 1% of tungsten have a negligible effect. Titanium above about 0.01 % causes significant interference.

The procedure based on the use of acid pyrogallol solution is suitable for determining tantalum over the range 2 to 7% in zirconium and niobium. The differential procedure is recommended for determining larger amounts of tantalum. In the presence of niobium or impurity amounts of iron, a correction must be applied. Zirconium does not interfere. Amounts up to about 5% of copper, aluminium or nickel, or 0.2% of tungsten have a negligible effect. Titanium above about 0.01% causes serious interference. The effect of molybdenum can be overcome by making a preliminary separation of tantalum (or niobium) with ammonium hydroxide.

In the determination of niobium or tantalum up to about 5%, the precision of the method is of the order ± 0.05%.

About 12 determinations can be made in a normal working day by one analyst.

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SUMMARY

Recent developments in the metallurgy of niobium, tantalum and zirconium have necessitated provision of analytical procedures for determining niobium and tantalum in the presence of each other and in the presence of zirconium. For this purpose, absorptiometric procedures based on the formation of yellow coloured complexes, between pyrogallol and niobium or tantalum, have been critically examined. Direct absorptiometric procedures are described, which are suitable for determining niobium or tantalum in the range 2 to 7%; when either of these metals exceeds 7%, differential absorptiometric procedures are recommended. Corrections must be made for absorption due to the presence of other metals which form complexes with pyrogallol. In the determination of niobium or tantalum up to 5%, the precision of the method is about ±0.05%. About 12 determinations can be made in a day, by one analyst.

RÉSUMÉ

Après une étude critique, des méthodes absorptiométriques rapides sont proposées pour le dosage du niobium, en présence de tantale et de ziconium et pour le dosage du tantale, en présence de niobium et de zirconium. Ces procédés sont basés sur la formation de complexes jaunes de ces éléments avec le pyrogallol. Des corrections doivent être faites en présence d'autres métaux formant des complexes avec ce réactif.

ZUSAMMENFASSUNG

Es werden „absorptiometrische" Methoden beschrieben zur raschen Bestimmung von Niob in Gegenwart von Tantal und Zirkonium sowie für Tantal in Gegenwart der beiden anderen Metalle. Die Grundlage der Methode beruht auf der Komplexbildung dieser Metalle mit Pyrogallol. Sind ausserdem noch andere Metalle vorhanden, die mit Pyrogallol Komplexe bilden, muss ein Korrektionsfaktor angewandt werden.

References p. 135

REFERENCES

1 W. R. Schoeller and A. R. Powell, *The Analysis of Minerals and Ores of the Rarer Elements*, Griffin, 1940.
2 R. N. Atkinson, J. Steigman and C. F. Hiskey, *Anal. Chem.*, 24 (1952) 480.
3 R. A. Mercer and A. F. Williams, *J. Chem. Soc.*, (1952) 1497.
4 R. A. Mercer and R. A. Wells, *Analyst*, 79 (1954) 339.
5 J. R. Werning and K. B. Higbie, *Ind. Eng. Chem., Anal. Ed.*, 46 (1954) 2491.
6 G. W. C. Milner and J. W. Edwards, *Anal. Chim. Acta*, 13 (1955) 230.
7 Yu. Chernikhov, R. S. Tramm and K. S. Pevzner, *Zavodskaya Lab.*, 22 (1956) 637.
8 G. Norwitz, M. Codell and F. Verderame, *Anal. Chim. Acta*, 9 (1953) 561.
9 A. O. E. Marzys, *Analyst*, 80 (1955) 194.
10 I. Geld and J. Carrol, *Analyst*, 21 (1949) 1098.
11 B. Sarma and J. Gupta, *J. Indian Chem. Soc.*, 32 (1955) 285.
12 M. S. Platonov and N. F. Krivoshlykov, *Trudy Vsesoyuz. Konf. Anal. Khim.*, 2 (1943) 359; *Analyst* (Abstracts) 73 (1948) 175.
13 E. C. Hunt and R. A. Wells, *Analyst*, 79 (1954) 345.

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A HIGHLY ACCURATE AND PRECISE METHOD FOR THE ASSAY OF CHROMIUM METAL AND CHROMIUM(III) OXIDE

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Because the magnitude of ordinary analytical errors is too high to provide the desired accuracy with precision, the direct assay of high purity materials is often avoided in favor of the determination of suspected minor contaminants. The usual practice of estimating the purity of such materials by difference after quantitative spectrographic analysis provides only an incomplete assay because several common impurities, such as oxygen, nitrogen, sulfur, and the halogens, are not readily amenable to spectrographic measurement.

In the case of high-purity chromium metal and chromium(III) oxide, a direct assay method has been developed which is suitable for routine use and capable of an accuracy and precision well within one part in a thousand. The procedure employs the addition of a weighed excess of solid ferrous ammonium sulfate hexahydrate to a sample solution which has been oxidized to the hexavalent state. The excess ferrous ion is then measured by amperometric titration[1]. Although a previous study[2] indicated that reagent-grade Mohr's salt can be obtained commercially which possesses a reducing power which is 99.8% of its theoretical strength, the optimum accuracy is assured by a preliminary assay of the ferrous ammonium sulfate hexahydrate against primary-standard-grade potassium dichromate using the same amperometric procedure.

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In order to check the accuracy of results obtained using Mohr's salt, the purity of the chromium metal employed was determined using primary-standard arsenic trioxide as reductant. Excess arsenite was measured by potentiometric titration. Comparison with respect to accuracy and precision indicated that either method could be used. However, with respect to operational simplicity, the Mohr's-salt reductant, used in conjunction with the amperometric titration, was much to be preferred.

EXPERIMENTAL

Apparatus

The equipment used in the amperometric titration has been previously described in the study made of the purity of Mohr's salt[2].

A Leeds and Northrup A.C. Operated pH Indicator (7664-Al), in conjunction with the appropriate platinum electrode and calomel reference electrode, was used to perform the potentiometric titrations where comparison was made with the arsenic trioxide method.

Reagents and solutions

The primary standards, potassium dichromate and arsenic trioxide, were obtained from the Mallinckrodt Chemical Works.

The ferrous ammonium sulfate hexahydrate was also supplied by Mallinckrodt (Analytical Reagent #5068). Assay against primary-standard dichromate indicated its reducing strength to be 99.87% ± 0.022 of the theoretical value[2].

The 0.0200 *N* solution of potassium dichromate was prepared directly from the primary-standard material.

A 0.05 *N* solution of ceric ammonium sulfate was prepared from the dihydrate, and standardized against primary-standard arsenic trioxide using osmium tetroxide as catalyst[3].

All other chemicals used were of reagent-grade quality. These, or the solutions prepared from them, include: ammonium persulfate, sulfuric acid 96%, perchloric acid 72%, sulfuric acid 1 : 1, nitric acid 1 : 1, sulfuric acid 3 *N*, sodium hydroxide 3 *N*, silver nitrate solution 5%, osmium tetroxide solution 0.01 *M* in 0.1 *M* sulfuric acid.

Procedure for the dissolution of samples and oxidation of chromium to the hexavalent state

Approximately 0.5 g of chromium metal, accurately weighed to the nearest 0.1 mg, was dissolved by heating *gently* with 30 ml of sulfuric acid, 1 : 1, in a 600-ml beaker Either powdered metal, or larger pieces, dissolved readily in this reagent after a short induction period. The induction period can be avoided by "grinding" the pieces with a stirring rod to initiate the reaction. After complete dissolution, the solution was brought to a volume of about 250 ml with distilled water.

The chromium(III) oxide samples were converted to chromic acid by the action of hot concentrated perchloric acid[4]. An accurately weighed sample of approximately 0.5 g was placed in a dry 600-ml beaker, and covered with 20 ml of a 1 : 1 mixture of perchloric acid (72%) and concentrated sulfuric acid. After heating for about 20 min at the fuming point, the sample was completely oxidized to chromic acid; and, after cooling, the chromic acid was dissolved in about 250 ml of distilled water.

Subsequently, sample solutions prepared from either the metal or the oxide were treated with ammonium persulfate to effect complete oxidation to dichromate. In accord with the recommendations of HILLEBRAND *et al.*[5], 6 ml of nitric acid, 1 : 1, were added, and the solutions brought to a boil before the addition of 10 ml of the silver nitrate solution (5%). After boiling resumed, ammonium persulfate was added cautiously from a scoop as the solid reagent, in portions each weighing 1–2 g. Repeated additions, after intervals of boiling, were required to completely oxidize the chromium at these high concentrations. The addition of ammonium persulfate in solution form was found to be impractical, and often led to incomplete oxidation which was difficult to observe visually. Solid reagent can be added in considerable excess (as much as 15 g) without adversely increasing the volume of the solution. In the case of the samples of chromium(III) oxide, a lesser amount of persulfate was required because chromium was partially oxidized by the perchloric acid treatment used for dissolution. After the last addition of persulfate, the solutions were boiled for 10 min to destroy excess persulfate. Hydrochloric acid can be added at this point to reduce manganese if its presence is suspected.

Procedure for the amperometric titration of the oxidized sample solutions

Titration of the oxidized solutions was accomplished in the same manner as described in the assay of Mohr's salt against primary-standard potassium dichromate[2]. Based upon a preliminary calculation of the dichromate resulting from the oxidation of the sample (assuming 100% purity), solid ferrous ammonium sulfate hexahydrate was weighed accurately to the nearest milligram to provide an equivalent amount of reductant plus a 50 mg excess. The assayed strength of the Mohr's salt was used as a correction factor before this weighing. The weighed crystals were added directly to the cooled dichromate solution, and were dissolved by stirring magnetically, in approximately 5 min. Excess of ferrous ion was indicated by an anodic current at +1.0 V applied to the rotating platinum electrode *vs.* S.C.E. and was titrated amperometrically using the 0.0200 *N* solution of potassium dichromate. The purity of the sample was calculated using the appropriate mequiv. weight from the net number of mequivs. of ferrous ammonium sulfate consumed by the oxidized sample solution.

Procedure for the titration of oxidized solutions using arsenic trioxide and a potentiometric end-point

In the comparison method, where arsenic trioxide was used as the reductant, a calculated amount of primary-standard-grade solid arsenic trioxide was weighed to provide an excess of about 0.2 mequivs. greater than the equivs. of chromium to be measured. Using extreme care to prevent loss of arsenic trioxide, the weighed oxide was transferred to a covered 150-ml beaker and dissolved by the addition of 20 ml of 3 *N* sodium hydroxide. The caustic arsenite solution was then neutralized with 3 *N* sulfuric acid. Reduction of either a solution of an exact weight of potassium dichromate or of an oxidized sample was accomplished by the addition of the neutralized arsenite solution. After stirring magnetically for 15 min, the excess arsenite was titrated potentiometrically, (calomel *vs.* anodized platinum electrodes), with 0.05 *N* ceric ammonium sulfate in the presence of 3 drops of 0.01 *M* osmium tetroxide catalyst. The platinum electrode used for the potentiometric titrations was anodized by making it the anode in 5% sulfuric acid for 15 sec with an applied voltage of 4 V.

RESULTS

Twelve replicate determinations of high purity chromium metal are listed in Table I along with the average purity of the metal and the 99% confidence limits of this average. The precision of the determination was estimated from the standard deviation to be about 3 parts in ten thousand with a 99% upper confidence limit of about 5 parts in ten thousand. This variability was in excellent agreement with that obtained using primary-standard potassium dichromate[2].

Table II shows the results of four replicate determinations of two samples of chromium trioxide. In the case of sample A the estimate of the standard deviation was in good agreement with that previously found. However, because a fewer number of replicates were taken, the confidence limits necessarily are less rigorous. In the case of sample B the standard deviation was twofold greater than that previously obtained. It is obvious that the first result listed for this sample is influencing this estimate of precision and therefore less confidence can be placed upon the average if this datum is included. However, because no obvious reason for rejecting this result was noted, other than variable sampling technique, it has been included in Table II.

Preliminary work with arsenic trioxide, as a primary standard reductant for dichromate, was carried out on solutions of primary standard potassium dichromate where such variables as the condition of the platinum electrode and the influence of silver nitrate was investigated. Table III summarizes the finding of this study where results are calculated in terms of the purity of the potassium dichromate, assuming 100.00% purity for arsenic trioxide. The need to anodize the platinum electrode was evident from the shape of potentiometric titration curves which were skewed when no prior anodizing was performed. Accordingly, the first two results reported were slightly higher than those found when the electrode was anodized. The effect of silver nitrate, although not rigorously evaluated, appears to have a slight influence causing a bias toward a higher result as indicated by the last two data in Table III.

TABLE I

ASSAY (IN %) OF HIGH PURITY CHROMIUM USING STANDARDIZED SOLID FERROUS AMMONIUM SULFATE HEXAHYDRATE

Grams chromium		*% purity*
taken	*found*	
0.5387	0.53875	100.01
0.4811	0.48065	99.92
0.4960	0.49596	99.99
0.5619	0.56177	99.98
0.5427	0.54263	99.99
0.4810	0.48084	99.97
0.5321	0.53180	99.94
0.5825	0.58232	99.97
0.4874	0.48740	100.00
0.3787	0.37844	99.93
0.4933	0.49319	99.98
0.4737	0.47353	99.96
Average		99.970
99% Confidence limits of average		99.945–99.995
Standard deviation of an individual measurement		±0.028 ($N = 12$)
99% Upper confidence limit of the standard deviation		0.053

References p. 140

TABLE II

PURITY OF CHROMIUM TRIOXIDE SAMPLES

	% *Purity* Cr_2O_3	
	Sample A	*Sample B*
	99.00	99.11
	99.10	99.41
	99.00	99.32
	90.06	99.32
Average	99.04	99.29
95% Confidence limits of average	98.95–99.13	99.08–99.50
Standard deviation[a] of an individual measurement	±0.055	0.13
95% Upper confidence limit of the standard deviation	0.16	0.38

[a] $N = 4$

TABLE III

THE COMPARISON OF PRIMARY-STANDARD ARSENIC TRIOXIDE[a] *versus* PRIMARY-STANDARD POTASSIUM DICHROMATE[b] BY POTENTIOMETRIC TITRATION

Grams $K_2Cr_2O_7$		% *purity* $K_2Cr_2O_7$
taken	*found*	
1.4082	1.4100	100.13[c]
1.4174	1.4193	100.13[c]
1.4137	1.4142	100.04[d]
1.4010	1.4012	100.02[d]
1.4172	1.4182	100.07[e]
1.4189	1.4197	100.06[e]

[a] Obtained from Mallinckrodt Chemical Works. Reported assay on label 99.95–100.05% As_2O_3.

[b] Obtained from Mallinckrodt Chemical Works. Reported assay on label 99.95–100.05% $K_2Cr_2O_7$.

[c] Electrodes were not anodized between titrations and silver was not added to the solution.

[d] Electrodes were anodized, silver was not added to the solution.

[e] Electrodes were anodized, silver added to the solution.

TABLE IV

ASSAY OF HIGH PURITY CHROMIUM USING ARSENIC OXIDE[a] AS REDUCTANT

Grams chromium		% *purity*
taken	*found*	
0.6471	0.64734	100.04
0.5366	0.53671	100.02
	Average = 100.03[b]	

[a] Assay of arsenic oxide calculated from data in Table III was 99.95% As_2O_3 assuming primary-standard potassium dichromate to be 100.00%.

[b] Compare with value of 99.970% shown in Table I.

Table IV shows duplicate results by the arsenic trioxide method for the analysis of the chromium metal previously assayed using ferrous ammonium sulfate. In order to facilitate comparison with the result previously shown in Table I, where potassium dichromate was the primary-standard reference material, the purity of the arsenic trioxide was calculated as 99.95% from the data in Table III (excluding the first two data). The agreement between methods (99.97% *vs.* 100.03%) was well within the desired accuracy and precision.

DISCUSSION AND CONCLUSIONS

Excellent results were obtained in the analysis of chromium by the use of solid, ferrous ammonium sulfate hexahydrate as a reductant in conjunction with an amperometric end-point. The accuracy and precision of the method were shown to be well within one part per thousand.

Reliable results were also obtained using the arsenic trioxide method. However, it possesses inherently a number of slow steps. These include the precautions which one must take in weighing the oxide (because of its comparatively low gravimetric factor), dissolving it prior to addition to the dichromate, and the subsequent potentiometric end-point, which must be estimated by dropwise additions of ceric ammonium sulfate. In addition, the platinum electrode should be anodized before each titration. By comparison, the amperometric end-point is considerably more rapid where only 6 additions of titrant provide a suitable end-point.

SUMMARY

A method capable of a precision of 3 to 5 parts in ten thousand has been developed for the routine assay of high purity chromium metal and chromium trioxide. Use has been made of the favorable gravimetric factor of ferrous ammonium sulfate and of an amperometric end-point. Comparison with the arsenic trioxide method was made.

RÉSUMÉ

Une méthode est proposée pour l'analyse du chrome métallique très pur et de l'oxyde de chrome(III). On utilise comme réactif le sulfate double de fer(II) et d'ammonium hexahydraté, dont on détermine l'excès par titrage ampérométrique.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Analyse von sehr reinem Chrommetall und Chrom-(3)-oxyd mit Eisen-(2)-Ammoniumsulfat-hexahydrat, dessen Überschuss durch ampèrometrische Titration bestimmt wird.

REFERENCES

[1] T. D. PARKS AND L. LYKKEN, *Anal. Chem.*, 22 (1950) 1503.

[2] H. J. KEILY, A. ELDRIDGE AND J. O. HIBBITS, *Anal. Chim. Acta*, 21 (1959) 6.

[3] I. M. KOLTHOFF AND E. B. SANDELL, *Textbook of Quantitative Inorganic Analysis*, 3rd Ed., Macmillian, New York, 1952, p. 583.

[4] G. F. SMITH, *Mixed Perchloric, Sulfuric and Phosphoric Acids and Their Applications in Analysis*, 2nd Ed., The G. Fredric Smith Chemical Company, Columbus, Ohio, 1942, p. 4.

[5] W. F. HILLEBRAND, G. E. F. LUNDELL, M. S. BRIGHT AND J. I. HOFFMAN, *Applied Inorganic Analysis*, 2nd Ed., John Wiley and Sons, New York, 1952, Chapter 33, p. 529.

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A SYSTEMATIC STUDY OF INSOLUBLE SUBSTANCES

IV. A SIMPLIFIED SCHEME FOR THE DETECTION OF ALL TYPES OF INSOLUBLE SUBSTANCES

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In the previous papers[1] of this series it has been shown that a large number of compounds become almost insoluble in acids after being heated at a high temperature for 2–9 h and thus must be categorized as 'insoluble substances'. An important problem to be considered is the detection of these compounds in qualitative analysis. The previous method of detecting the insoluble substances (which has been dealt with in two earlier papers[2,3]) is convenient when the number of such substances is comparatively small and limited. With the addition of a very large number of substances to this category — and the number of such substances is likely to be continuously increased — it is necessary that a scheme be devised which has a universal character and can provide for the detection of all types of insoluble substances that have already been added or may be added in the future.

As the provided increase in the number of insoluble substances is likely to make the scheme for their detection more and more complicated, it has been found necessary to combine this scheme with the schemes used for the detection of anions[4] as well as of cations[5]. In this way many of the insoluble substances are removed and form part both of the sodium carbonate filtrate used in the detection of anions and the acid solution used for the detection of cations.

Further simplification of the scheme for the detection of the insoluble substances is possible by taking the product of fusion with $KOH + K_2CO_3 + KNO_3$, dividing the large number of basic radicals present in it into different groups with various reagents and combining these groups with the corresponding groups obtained in the main scheme for the basic radicals[5]. In this way duplication of work and waste of time is avoided in the systematic analysis of two separate solutions containing practically the same elements. The manner in which the product of fusion with $KOH + K_2CO_3 + KNO_3$ is divided into different groups by various reagents and the solutions thus obtained are combined with the corresponding groups of the systematic scheme for the basic radicals is shown in Tables I and II.

The new scheme which is meant to provide for all types of insoluble substances will be seen to differ from the previous scheme[2,3] in the following ways:

(1) The mixture is treated first with sodium carbonate solution to remove the large majority of anions. This also removes a number of substances which otherwise might have formed part of the insoluble residue; *e.g.* ferrocyanides, ferricyanides, nitroprussides (form ferrocyanides), sulphates of lead and strontium, manganese phosphate and the oxides of molybdenum and tungsten. For instance, a substance like $SrSO_4$

TABLE I

<table>
<tr><td colspan="4">Boil 2–3 g of the mixture with 8–10 g of sodium carbonate (AnalaR quality) in about 100 ml of water for 10 min. Filter.</td></tr>
<tr><td colspan="3">Residue: Hydroxides of Th, Cr, Fe, Cu, Co, Ni, Mn, $Na_2U_2O_7$; carbonates of Pb, Ba, Sr, Ca etc. and other soluble and insoluble contents of the mixture. Subject it to the acid treatments (Procedure I)[5]; take up with dil. HCl, filter and wash with hot water.</td><td rowspan="3">Filtrate: Almost all the anions and certain basic radicals.
Analyse according to the scheme for anions[4].</td></tr>
<tr><td colspan="2">Residue: The following insoluble compounds will be present in addition to all the insoluble substances for alkaline fusion mentioned in a previous paper[3] (—$SrSO_4$ + $CrCl_3$)[a].
Phosphate of Cr; Arsenates of Zr, Ti, Cr and Sn; Antimonates of Cu, Zn, Cd, Mn, Co, Ni, Mg, Cr, Be, Ca, Sr, Ba, Al, Th, Zr and U; Chromites of Be, Mg, Zn, Cd, Cu, Co, Ni, Mn, Zr, Ce and U; Aluminates of Cu, Zn, Co, Ni and Mn; Tungstates of Cu, Co, Ni, Zn, Cr and Zr; Tellurates of Cr and Zr; Vanadates of Cr and Zr; Chloride of Ag; and H_2WO_4 derived from the insoluble tungstates and tungsten metal.
Treat with NH_4OH solution and filter.</td><td rowspan="2">Filtrate: All the basic radicals.
Analyse according to the scheme for basic radicals[5].</td></tr>
<tr><td>Residue: All the above mentioned compounds with the exception of AgCl and H_2WO_4.
Fuse with a large excess of a fusion mixture consisting of KOH + K_2CO_3 + KNO_3 in a nickel crucible over a blow-pipe flame.
The following reactions take place:</td><td>Filtrate: Ammonium tungstate and silver–ammonia complex.
Test for W and Ag in usual fashion.</td></tr>
</table>

Zirconium tellurate $\downarrow$ Zirconium tellurate

Chromium tellurate $\downarrow$ $K_2CrO_4 + K_2TeO_4$

Zinc chromite $\longrightarrow K_2CrO_4 + K_2ZnO_2$

Beryllium chromite $\longrightarrow K_2CrO_4 + K_2BeO_2$

Magnesium chromite $\longrightarrow MgO + K_2CrO_4$

Cadmium chromite $\longrightarrow CdO + K_2CrO_4$

Copper chromite $\longrightarrow CuO + K_2CrO_4$

Cobalt chromite $\longrightarrow CoO + K_2CrO_4$

Nickel chromite $\longrightarrow NiO + K_2CrO_4$

Manganese chromite $\longrightarrow MnO_2 + K_2CrO_4$

Zirconium chromite $\longrightarrow K_2ZrO_3 + K_2CrO_4$

Cerium chromite $\longrightarrow CeO_2 + K_2CrO_4$

Uranium chromite $\longrightarrow K_2U_2O_7 + K_2CrO_4$

Zinc aluminate $\longrightarrow KAlO_2 + K_2ZnO_2$

Copper aluminate $\longrightarrow CuO + KAlO_2$

Cobalt aluminate $\longrightarrow CoO + KAlO_2$

Nickel aluminate $\longrightarrow NiO + KAlO_2$

Manganese aluminate $\longrightarrow MnO_2 + KAlO_2$

Chromium tungstate $\longrightarrow K_2WO_4 + K_2CrO_4$

Zirconium tungstate $\longrightarrow K_2ZrO_3 + K_2WO_4$

Zinc tungstate $\longrightarrow K_2WO_4 + K_2ZnO_2$

Copper tungstate $\longrightarrow CuO + K_2WO_4$

Nickel tungstate $\longrightarrow NiO + K_2WO_4$

Cobalt tungstate $\longrightarrow CoO + K_2WO_4$

$K_2ZnO_2 + K_3SbO_4 \longleftarrow$ Zinc antimonate

$K_2BeO_2 + K_3SbO_4 \longleftarrow$ Beryllium antimonate

$K_2CrO_4 + K_3SbO_4 \longleftarrow$ Chromium antimonate

$KAlO_2 + K_3SbO_4 \longleftarrow$ Aluminium antimonate

$K_3SbO_4 + MgO \longleftarrow$ Magnesium antimonate

$K_3SbO_4 + CdO \longleftarrow$ Cadmium antimonate

$K_3SbO_4 + MnO_2 \longleftarrow$ Manganese antimonate

$K_3SbO_4 + CoO \longleftarrow$ Cobalt antimonate

$K_3SbO_4 + NiO \longleftarrow$ Nickel antimonate

$K_3SbO_4 + CuO \longleftarrow$ Copper antimonate

$K_3SbO_4 + CaCO_3 \longleftarrow$ Calcium antimonate

$K_3SbO_4 + SrCO_3 \longleftarrow$ Strontium antimonate

$K_3SbO_4 + BaCO_3 \longleftarrow$ Barium antimonate

$K_3SbO_4 + ThO_2 \longleftarrow$ Thorium antimonate

$K_3SbO_4 + K_2ZrO_3 \longleftarrow$ Zirconium antimonate

$K_3SbO_4 + K_2U_2O_7 \longleftarrow$ Uranium antimonate

$K_3AsO_4 + K_2ZrO_3 \longleftarrow$ Zirconium arsenate

$(K_2TiO_3) + K_3AsO_4 + TiO_2 \longleftarrow$ Titanium arsenate

$K_2CrO_4 + K_3AsO_4 \longleftarrow$ Chromium arsenate

$K_2SnO_3 + K_3AsO_4 \longleftarrow$ Tin arsenate

$K_2CrO_4 + K_3VO_4 \longleftarrow$ Chromium vanadate

$K_3VO_4 + K_2ZrO_3 \longleftarrow$ Zirconium vanadate

$KCl + K_2CrO_4 \longleftarrow$ Chromium chloride

$K_3PO_4 + K_2CrO_4 \longleftarrow$ Chromium phosphate

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[a] $SrSO_4$ is completely decomposed by boiling with 10% sodium carbonate solution and will not be present here. Anhydrous $CrCl_3$ is only partially decomposed by boiling with 10% sodium carbonate solution and aqua regia and will therefore be present here.

TABLE II

<table>
<tr><td colspan="9">Crush and digest the fused mass with 1 N K_2CO_3 solution at which point all the compounds enclosed within the lines will pass into solution. Filter.</td></tr>
<tr><td colspan="3">Residue: MgO, NiO, MnO_2, CoO, CuO, CdO, K_2ZrO_3, TiO_2, $K_2U_2O_7$, IrO_2, $SrCO_3$, $BaCO_3$, $CaCO_3$, CeO_2, ThO_2, RhO_2, zirconium tellurate and oxides of Sc, Y, La and rare earths.
Boil with conc. HCl and conc. HNO_3 mixed in the proportions of 5 : 1.
Evaporate nearly to dryness, add dil. HCl to the residue and filter.</td><td colspan="6">Filtrate: K_2RuO_4, K_2WO_4, $K_8Nb_6O_{19}$, $K_8Ta_6O_{19}$, K_3SbO_4, K_3AsO_4, K_2SnO_3, K_2TeO_4, K_3PO_4, $KAlO_2$, K_2ZnO_2, K_2BeO_2, K_2CrO_4, K_2SiO_3, K_2TiO_3, K_3VO_4, K_2SO_4, KCl and KF. Divide it into two parts.
(1) Test for SO_4^{-2}, PO_4^{-3}, Cl^- and F^-.
(2) Make strongly acid with conc. HCl, evaporate to a small volume, add dil. HCl and filter.</td></tr>
<tr><td colspan="2" rowspan="3">Residue: CeO_2, ThO_2, RhO_2 and zirconium tellurate. Fuse with $KHSO_4$ in a silica crucible to convert them into sulphates. Dissolve the fused mass in dil. HCl. Treat with 2 N Na_2S reagent in excess followed by conc. HCl and 10–15 g of CH_3COONH_4 (solid) Boil to precipitate the sulphides of Rh and Te as completely as possible. Filter.</td><td rowspan="4">Filtrate: Chlorides of Mg, Ni, Mn, Co, Cu, Cd, Zr, Ti, U, Ir, Sr, Ba, Ca and Sc, Y, La and rare earths.
Mix it with the acid extract for the detection of basic radicals, (Procedure II)[5].</td><td colspan="2">Precipitate: $WO_3 \cdot H_2O$; $SiO_2 \cdot H_2O$ and Ta_2O_5. Treat with NaOH solution and filter.</td><td colspan="4">Filtrate: Chlorides of Ru, Nb, Ti, Al, Cr, Be, Zn, Sn, Sb and acids of Te, As and V. Treat with 4 N NaOH solution to neutralize most of the free acid but keeping the solution still acidic. Then use 2 N Na_2S reagent followed by 4–5 g of CH_3COONH_4 (solid) and Na_2CO_3. Filter.</td></tr>
<tr><td rowspan="3">Ppt. Ta_2O_5. Test for Ta as usual</td><td rowspan="3">Filtrate: Na_2WO_4 and Na_2SiO_3.
Test for W and Si as usual.</td><td colspan="3">Precipitate Ru_2S_3, $Al(OH)_3$, $Cr(OH)_3$, $Be(OH)_2$, ZnS, $Ti(OH)_4$, and $Nb(OH)_5$. Treat with cold dil. HCl and filter.</td><td rowspan="3">Filtrate: Thiosalts of Te, As, Sn, Sb and V.
Mix with the thiosalt group (Procedure III)[5].</td></tr>
<tr><td rowspan="2">Ppt. Brown Ru_2S_3 shows Ru.</td><td colspan="2">Filtrate: Chlorides of Ti, Nb, Al, Cr, Be and Zn. Treat with excess of NaOH + Na_2O_2 and Na_2CO_3. Boil to decompose excess of Na_2O_2 and filter.</td></tr>
<tr><td>Precipitate: Sulphides of Rh and Te. Mix with the sulphides of arsenic group (Table II)[5].</td><td>Filtrate: Chlorides of Zr, Ce and Th. Boil off H_2S completely and mix the solution with iron and rare earths group solution (Procedure VI)[5].</td><td>Precipitate: $Ti(OH)_4$ and $Nb(OH)_5$. Test for Ti and Nb as usual (Table II)[3].</td><td>Filtrate: $NaAlO_2$, Na_2CrO_4, Na_2BeO_2 and Na_2ZnO_2. Mix it with the aluminium group (Table V)[5].</td></tr>
</table>

is decomposed completely by boiling with concentrated sodium carbonate solution. The sulphate passes into the sodium carbonate filtrate, $SrCO_3$ dissolves in the acid treatment and thus the insoluble residue does not contain $SrSO_4$. Another advantage is that a number of complex salts, like phosphotungstic acid, which dissolve in the standard acid treatment and complicate the analysis of this solution for basic radicals, pass completely into the sodium carbonate filtrate and are quite easily detected in this solution.

By this removal of many substances such as lead sulphate, ferrocyanides, ferricyanides, nitroprussides and the oxides of molybdenum and tungsten, it is possible to do away with Procedures I and II[2] which involve treatment with a saturated ammonium acetate solution and 4 *N* caustic soda solution respectively. The insoluble residue left after the acid treatment is treated only with NH_4OH solution for the removal of silver chloride and tungstic acid and then fused with $KOH + K_2CO_3 + KNO_3$. The treatment of the insoluble residue is thus greatly simplified and consists mainly of two operations; namely, fusion with (a) $KOH + K_2CO_3 + KNO_3$ and (b) $KHSO_4$.

(2) The various solutions obtained in the treatment of the fused mass are combined with the different groups of the scheme for the basic radicals. Thus the whole of the solution obtained after the extraction of the fused mass (not dissolved in K_2CO_3 solution) with concentrated acids (Table II) is combined with the main solution for the detection of the basic radicals. In the treatment with the K_2CO_3 solution, at one stage the solution contains only the metals of the arsenic group; this is combined with the thiosalts-forming group of the main solution. At another stage a solution is obtained which contains only the metals of the aluminium group; this is combined with the aluminium group of the main solution. The detection of the insoluble substances thus involves only a few extra procedures of a comparatively simple nature owing to the amalgamation with the schemes for cations and anions. The new scheme may be taken as final because it will easily provide for any new insoluble substances that may be discovered.

Note

In the Table showing the behaviour of the insoluble substances on fusion with $KOH + K_2CO_3 + KNO_3$ only reactions of the newly discovered insoluble substances have been shown. The reactions of the other insoluble substances have already been demonstrated in an earlier paper[3]. In studying the behaviour of the insoluble substances on fusion with $KOH + K_2CO_3 + KNO_3$ both tables should be studied together.

SUMMARY

A simplified scheme for the detection of all types of insoluble substances has been proposed. This scheme is based on the amalgamation of the procedures employed in the detection of insoluble substances with the schemes for the detection of cations and anions and thus very considerably simplifies the procedures ordinarily applied.

RÉSUMÉ

Une méthode simplifiée d'identification de tous les types de substances insolubles est proposée.

ZUSAMMENFASSUNG

Es wird ein vereinfachtes Verfahren zur Identifizierung unlöslicher Verbindungen aller Typen beschrieben.

REFERENCES

[1] I. K. Taimni and I. S. Ahuja, *Anal. Chim. Acta*, 19 (1958) 492; 20 (1959) 119; 21 (1959) 3.
[2] I. K. Taimni and G. B. S. Salaria, *Anal. Chim. Acta*, 14 (1956) 4.
[3] G. B. S. Salaria, *Anal. Chim. Acta*, 19 (1958) 316.
[4] I. K. Taimni and Manohar Lal, *Anal. Chim. Acta*, 17 (1957) 367, 372, 21 (1959) 105.
[5] G. B. S. Salaria, *Anal. Chim. Acta*, 16 (1957) 509.

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TIRON AS A SPECTROPHOTOMETRIC REAGENT FOR THE ESTIMATION OF OSMIUM

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During the studies[1] on the spectrophotometric estimation of copper with tiron, the latter was found to give a reddish violet colour with osmium(IV) in the presence of sodium acetate. On the basis of this colour reaction, a method reported herein, for the estimation of osmium(IV), has been derived.

The coloured complex, with maximum and minimum absorptions at 470 mμ and 410 mμ, respectively, obeys Beer's law; the optimum range with the minimum error lies between 8 and 24 p.p.m. of osmium. The sensitivity of the reaction is 0.2 p.p.m., *i.e.*, 0.033 μg per cm^2 according to the definition of Sandell.

The sodium acetate, besides controlling the pH of the solution between 4.9 and 5.5 (the optimum region of complex formation), aids the colour development. For the full development of the colour, heating for a period of 15 min on a boiling water bath is essential. The colour so formed is stable for a period of 4 to 6 h. Longer periods slowly deepen the colour, and a higher pH shifts the maximum absorption region to a lower wavelength.

EXPERIMENTAL

Apparatus and solutions

Hilger's U.V. spectrophotometer was used for measuring the absorption of solutions in quartz absorption cells of 1-cm light path and with a tungsten filament lamp as the light source. Corrections, wherever necessary, were made to compensate for slight differences in the optical transmission of the cells.

pH measurements were made with a Cambridge pH indicator provided with an all-purpose (pH 1 – 13) glass electrode.

A weighed quantity of the chloro osmate (K_2OsCl_6) of Johnson and Matthey was dissolved in 1*N* hydrochloric acid solution. The final concentration of osmium per ml of the solution was 0.2 mg.

A 5% solution of the reagent, tiron, disodium salt of 1,2-dihydroxybenzene 3,5-disulphonate, was prepared in the same way as reported in an earlier paper[1].

A 5*N* solution of sodium acetate was prepared and used for adjusting the pH of the colour solution.

For the study of the effect of diverse ions, solutions of the ions were prepared from their reagent-grade samples.

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Spectral transmittancy

An aliquot portion of the solution of osmium, mixed with 5 ml each of the tiron and the sodium acetate solutions added successively, was diluted with water to a volume of 20 ml and heated on the boiling water bath for 15 min. After cooling in ice water, the solution was transferred to a 25-ml volumetric flask where its volume was made up with water. A reagent blank with 1% tiron and 1% sodium acetate was also prepared in exactly the same way as previously stated. Spectral transmittancies for the solutions prepared were then measured. Curves A and B in Fig. 1 show the transmittancy of 8 p.p.m. of osmium against water and reagent blanks, respectively, and curve C exhibits the absorbancy of the reagent against the water blank. From the figure it is quite clear that the maximum absorption of the color system was at 470 mμ, while the absorption is minimum at 410 mμ.

Effect of time, temperature, pH and reagent

Full development of colour, even in the presence of sodium acetate, takes place only when the solution is heated for about 15 min. In about 3 min time the colour just appears and in 15 min the intensity is maximum. Further heating has no effect. After such development, the colour, which remains practically at a constant intensity at room temperature for about 4 to 5 h, is usually measured. Over longer periods of time, the colour slowly deepens.

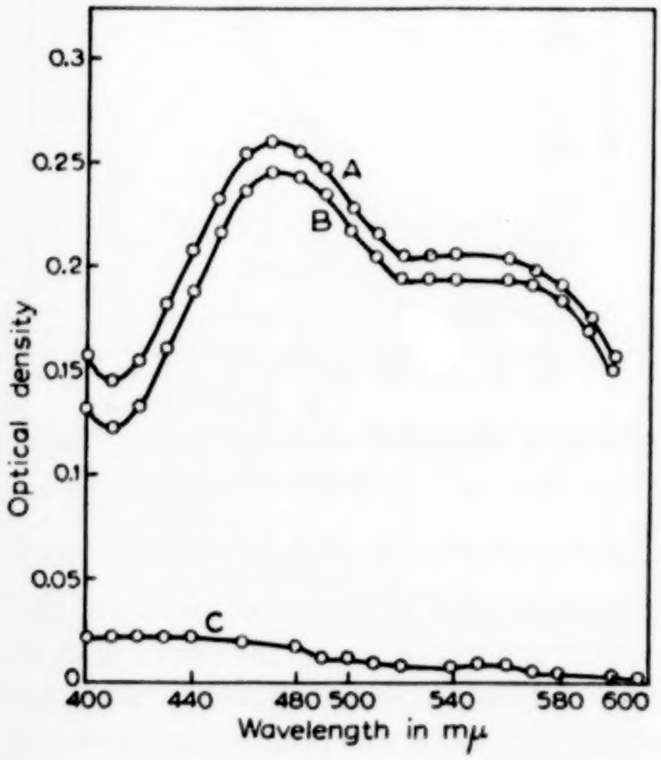


Fig. 1. Absorbance curves (A) 8 p.p.m. Os^{+4} against water blank; (B) 8 p.p.m. Os^{+4} against reagent blank; (C) Absorption of reagent against water blank.

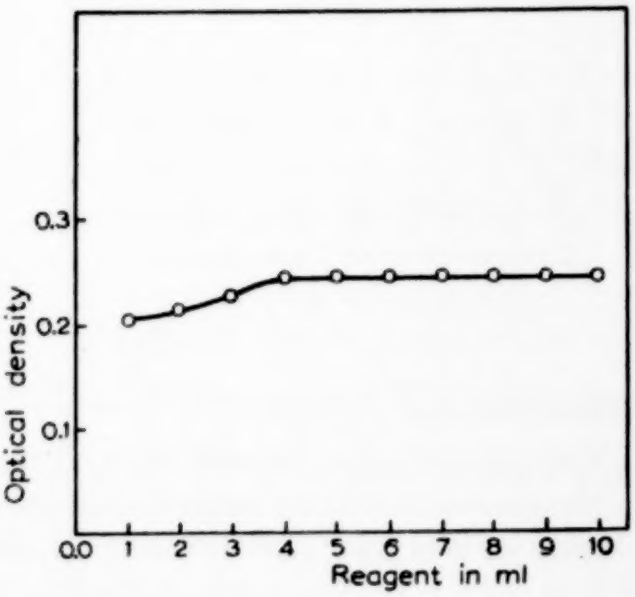


Fig. 2. Effect of reagent.

The nature and the maximum absorption region of the coloured complex being dependent on the pH, a thorough study of the effect of the latter justifies adjustment of the pH of the solution between 4.9 and 5.5, by sodium acetate. A pH higher than

5.5 decreases the intensity of the colour and changes the region of maximum absorption to a lower wavelength. The colour is not fully developed if the pH of the solution is maintained at a value lower than 4.9.

A study of the reagent concentration, on the colour system formed at pH 4.9 to 5.5, with different quantities (1 to 10 ml) of the reagent solution, added to 8 p.p.m. of osmium in solution in the manner described above, indicates (Fig. 2) that in a volume of 25 ml the amount of reagent required is only 4 ml. For all subsequent studies, 5 ml of the reagent were always used for a total volume of 25 ml.

Beer's law

For the study of the variation in O. D. with the concentration of osmium, solutions with different quantities of osmium(IV) were treated separately for their maximum colour development and their absorbancies were then measured at 470 mμ against a reagent blank. The curve in Fig. 3, obtained by plotting the O. D. against the concentration of osmium, from 2 to 32 p.p.m., is a perfect straight line passing through the origin. The molar extinction coefficient as calculated from Beer's law is 5706.

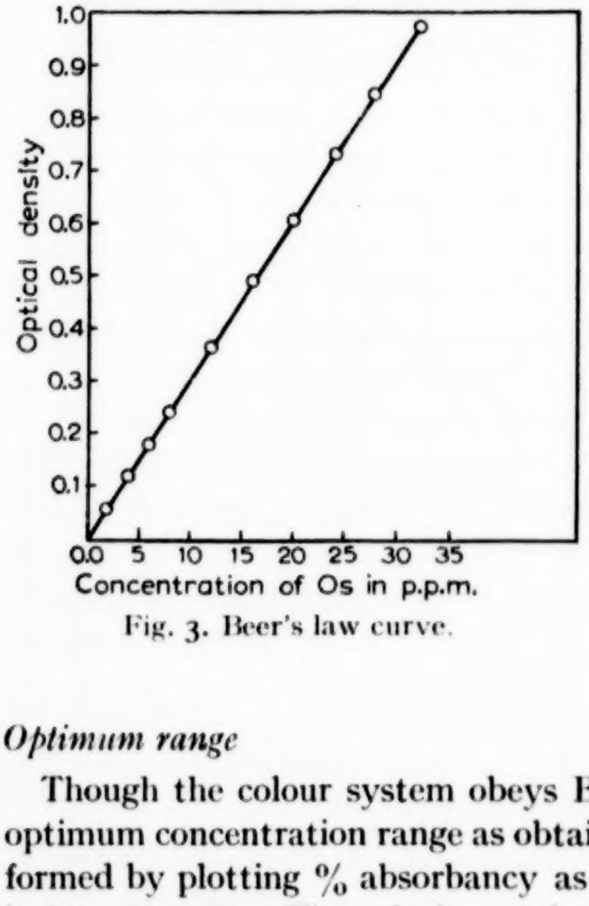


Fig. 3. Beer's law curve.

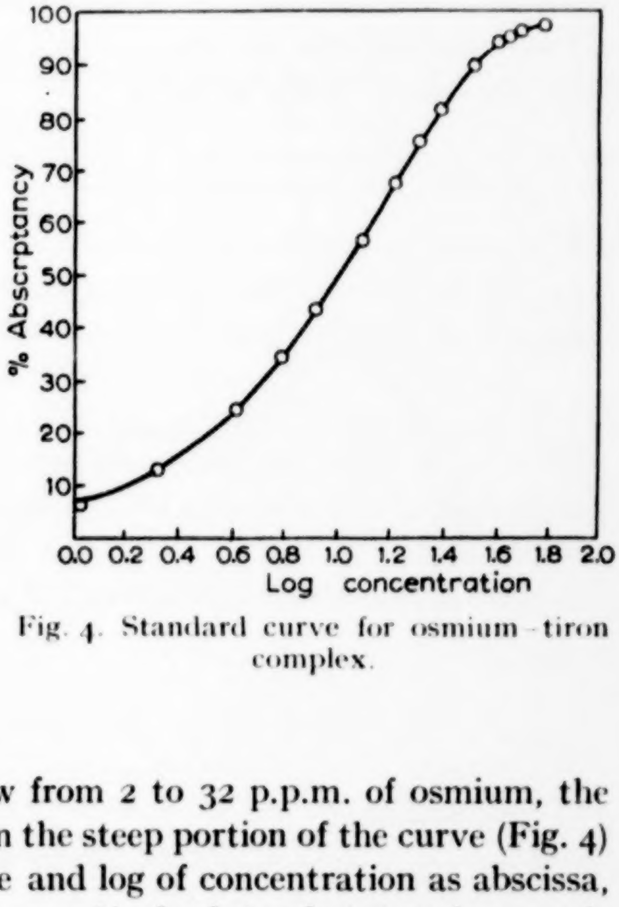


Fig. 4. Standard curve for osmium–tiron complex.

Optimum range

Though the colour system obeys Beer's law from 2 to 32 p.p.m. of osmium, the optimum concentration range as obtained from the steep portion of the curve (Fig. 4) formed by plotting % absorbancy as ordinate and log of concentration as abscissa, is 8 to 24 p.p.m. The relative analysis error per 1% absolute photometric error is 2.878%.

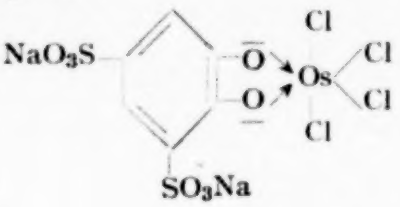
Effect of diverse ions

Fe^{+3}, Ti^{+4}, Nb^{+5}, Ta^{+5}, Ce^{+4}, UO_2^{+2}, CrO_4^{-2}, MoO_4^{-2}, OsO_4 and VO_3^- interfere by forming coloured complexes as do other platinum metals, except platinum itself. Ag^+ and Au^{+3} are reduced to metal, while Pt is tolerated to the extent of 10 times the amount of osmium. Al^{+3}, Ca^{+2}, Ba^{+2}, Sr^{+2}, Sn^{+4}, Pb^{+2}, Zr^{+4}, Th^{+4}, Hg^{+2} and WO_4^{-2}

are tolerated to a limited extent. Oxalate, citrate, tartrate, sulphate and phosphate are of no effect, but thiosulphate decolourizes the complex.

Composition

The composition of the complex was determined by the method of continuous variation and by the molar ratio method, according to the procedure reported in an earlier paper[1]. It was found that in solution, the complex was formed when the osmium and the reagent were in a ratio of 1:1 (*cf.* Figs. 5 and 6). Thus the complex can be represented structurally as



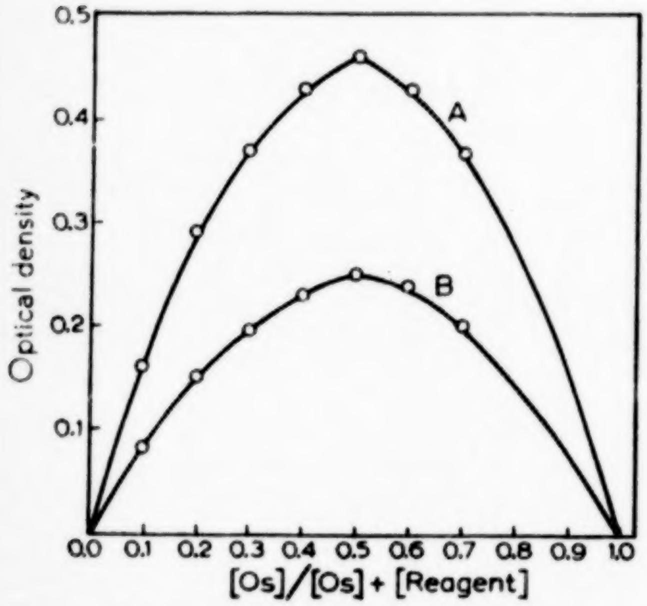


Fig. 5. Job's method of composition: (A) $1 \cdot 10^{-3} M$ solution, (B) $0.5 \cdot 10^{-3} M$ solution.

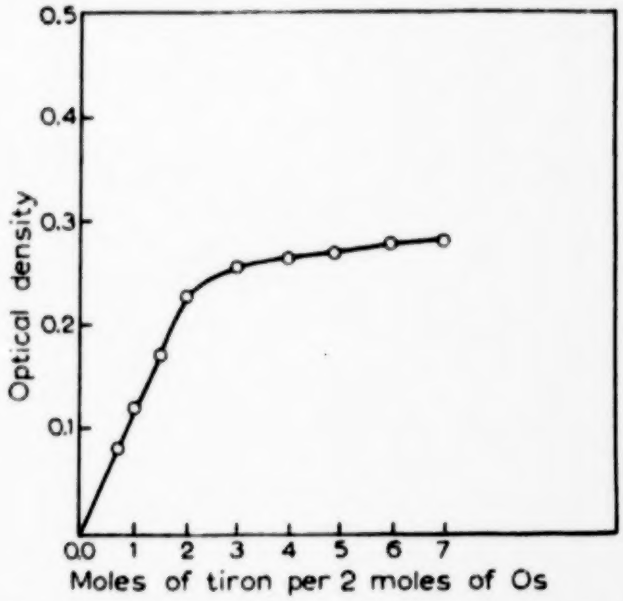


Fig. 6. Molar ratio method of composition $1 \cdot 10^{-3} M$ solutions.

Degree of dissociation and instability constant

With a solution $6.31 \cdot 10^{-5} M$ with respect to osmium, the degree of dissociation, α, was evaluated according to the equation[2] $\alpha = \frac{E_m - E_s}{E_m}$ and from this, K, the instability constant, was calculated from the relationship[2] $K = \frac{\alpha^2 c}{1 - \alpha} \cdot E_m$ and E_s values being equal to 0.360 and 0.145, respectively, K was found to be equal to $5.569 \cdot 10^{-5}$.

ACKNOWLEDGEMENT

Our grateful thanks are due to the University Grants Commission, Government of India, for providing us with the funds for the purchase of the Uvispek spectrophotometer and the Cambridge pH indicator.

SUMMARY

A method for the spectrophotometric determination of osmium with tiron as a reagent has been described. The reagent forms a soluble and stable coloured complex on heating with osmium in the presence of sodium acetate. The regions of maximum and minimum absorptions are at 470 mμ and 410 mμ, respectively, and the system obeys Beer's law from 2 to 32 p.p.m. of osmium. But the optimum range, with the relative analysis error of 2.878% per 1% absolute photometric error, is from 8 to 24 p.p.m. of osmium. The sensitivity of the reaction is 0.033 μg/cm^2 (SANDELL) and the molar extinction coefficient is 5706. In solution, the complex is formed when the osmium and the reagent are in a ratio of 1 : 1; it has an instability constant equal to approximately $5.57 \cdot 10^{-5}$.

RÉSUMÉ

Le tiron est proposé comme réactif pour le dosage spectrophotométrique de l'osmium. Le complexe rouge violet obtenu est stable. Absorption maximum à 470 mμ; sensibilité 0.033 μg/cm^2; coefficient d'extinction molaire 5706.

ZUSAMMENFASSUNG

Als Reagenz zur spektrophotometrischen Bestimmung von Osmium wird Tiron vorgeschlagen, das mit Osmium einen stabilen, rotviolett gefärbten Komplex bildet. Absorptionsmaximum bei 470 mμ; Empfindlichkeit: 0.033 μg/cm^2; molarer Extinktionskoeffizient: 5706.

REFERENCES

[1] A. K. MAJUMDAR AND C. P. SAVARIAR, *Anal. Chim. Acta*, 21 (1959) 53.

[2] A. E. HARVEY, JR. AND D. L. MANNING, *J. Am. Chem. Soc.*, 72 (1950) 4488; 74 (1952) 4744.

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THE DETECTION OF PRESERVATIVES IN WOOD WITH PYROCATECHOL VIOLET

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INTRODUCTION

The presence of preservatives in wood impregnated with water-soluble preservatives frequently cannot be detected visually because the salts are either colourless or masked by the natural colour of the wood. This masking effect is particularly so with the lower retentions used in the treatment of wood for use out of contact with the ground. In consequence, chemical spot tests have been developed to detect various preservative components in wood. FEIGL[1] has suggested tests for mercury, zinc, and copper salts as well as for sodium fluoride. The American Wood Preservers' Association[2] has proposed tests for copper, zinc and arsenic, while tests for the presence of boron have recently been reviewed by WILSON[3].

The preservatives used in New Zealand are zinc–copper–chrome–arsenate, copper–chrome–arsenate, fluoride–chrome–arsenate–phenol, acid copper chromate with or without boric acid and boric acid–borax mixtures. In this laboratory the tests given in Table I have been used to detect and identify these preservatives.

With the exception of the test for boron, however, these procedures are of little value in field testing, for the reagents are either too sensitive, occasionally giving tests which are positive on untreated samples, or because the reagent solutions are not stable for more than a few days. Further, to identify any of the current preservatives

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TABLE I

SPOT TESTS FOR THE IDENTIFICATION OF PRESERVATIVES IN WOOD

Reagent	*Preservative*					
	Zn–Cu–Cr–As	*Cu–Cr–As*	*NaF–Cr–As–DNP*	*Cu–Cr*	*Cu–Cr–B_2O_3*	*B_2O_3*
1% Dithizone in $CHCl_3$	Violet red	Deep brown	—	Deep brown	Deep brown	—
0.5 % Diphenyl carbazide in acetone	Violet pink	Violet pink	—	Violet pink	Violet pink	—
Molybdate[2] + benzidine + $SnCl_2$	Blue	Blue	Blue	—	—	—
Turmeric[3] + acid	—	—	—	—	Red	Red

requires at least three separate reagents, of which two are two-solution types. For these reasons field testing is infrequently used, and in practice samples are submitted to the laboratory for examination.

SUK AND MALAT[4] have described the properties of Pyrocatechol Violet (PCV). Since it gives colour reactions with many cations and some anions, notably borate, it seemed likely that this reagent might offer promise in the detection of preservatives. No reaction is, however, given by arsenic.

TABLE II

THE REACTION OF PYROCATECHOL VIOLET WITH VARIOUS IONS IN WOOD

Ion	*Retention as % ion in wood*				
	0.55	*0.28*	*0.15*	*0.07*	*0.04*
BO_3^{-3}	Brick-red	Red-brown	Brown-yellow	Green-yellow	Green-yellow
Cu^{+2}	Deep blue	Deep blue	Deep blue	Deep blue	Deep blue
Cr^{+6}	Deep blue	Deep blue	Deep blue	Blue green	Green-yellow
Cr^{+3}[a]	—	—	—	—	—
Zn^{+2}	Red-brown	Red-brown	Red-brown	Brown-yellow	Green-yellow

[a] All samples gave a deep blue colour after some hours

TABLE III

THE REACTION OF PYROCATECHOL VIOLET WITH PRESERVATIVES IN WOOD

Preservative	*Retention as % anhydrous salt*				
	4.60	*2.30*	*1.16*	*0.56*	*0.30*
Zn–Cu–Cr–As	Blue	Blue	Bluish-red	Red-brown	Red-brown
Cu–Cr–As	Blue	Blue	Blue	Blue	Blue
NaF–Cr–As–DNP[a,b]	—	—	—	—	—

[a] 2 : 4 Dinitrophenol
[b] Blue colour develops after some hours in all cases

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EXPERIMENTAL

Qualitative tests

It has been found that positive tests are obtained on *P.radiata* wood impregnated with Cu^{+2}, Cr^{+6}, Cr^{+3}, Zn^{+2} and BO$_3^{-3}$ when the reagent is applied as a 0.1% aqueous solution buffered with ammonium acetate. These results are shown in Table II, while results obtained on *P.radiata* impregnated with preservatives are given in Table III.

These tests are also obtained on freshly treated wood. Untreated wood assumes a yellow colouration with the reagent. The boron test tends to intensify over some hours, but the transitional concentration between a definite positive test and a negative test lies in the region of 0.30 to 0.15% boric acid in the oven-dry wood and is obtained immediately, as with the turmeric test. The boron complex is masked by mannitol. Fluoride enhances the colour of the boron test. Zinc–copper–chrome–arsenate contains only a small proportion of copper, and this accounts for the change in colour at the higher concentrations. Other concentrations and acidities of the reagent were also tested but these offered no advantage over the 0.1% solution in ammonium acetate.

As the reaction with metal ions is masked by ethylenediaminetetraacetic acid (EDTA), the possibility of estimating preservative loadings by additions of EDTA to the reagent mixture was studied and the results given in Table IV show this is certainly the case with copper–chrome–arsenate treated wood. The other preservatives were not studied in this respect.

TABLE IV

THE EFFECT OF EDTA ON THE PCV REACTION WITH COPPER–CHROME–ARSENATE

Reagent	*Retention as % anhydrous salt*				
	4.60	*2.30*	*1.16*	*0.56*	*0.30*
0.1% PCV + buffer	Blue	Blue	Blue	Blue	Blue
0.1% PCV + buffer + 0.05% EDTA	Blue	Blue	Blue	Blue-yellow	Yellow
0.1% PCV + buffer + 0.1% EDTA	Blue	Blue	Blue-yellow	Yellow	Yellow

Detection of arsenate and fluoride

SUK AND MALAT[4] state that molybdate, thorium and zirconium form blue complexes with Pyrocatechol Violet in acid solution. It has been found that this reaction is masked by arsenate, fluoride, and phosphate and only the red colour of the reagent in acid solution is obtained. Application of these facts to the detection of arsenate and fluoride in wood showed that an excellent indication of the presence of these anions is given with the zirconium compound, but the results were not absolutely unequivocal in the case of molybdate and thorium if copper was present, as, on standing, a gradual development of the blue copper complex tended to mask the reddish pink colour developed by the mixed reagent in the presence of the arsenate and fluoride. The zirconium complex forms in more acid solution (pH 1), and sufficient acid

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TABLE V

THE REACTION OF PCV–ZIRCONIUM COMPLEX WITH ARSENATE-CONTAINING WOOD

Reagents	*Retention as % As_2O_5 in wood*				
	5.0	*2.5*	*1.25*	*0.6*	*0.3*
0.05% PCV 0.05 $ZrOCl_2$ pH 1	Red	Red	Red	Red	Red
0.05% PCV 0.1% $ZrOCl_2$ pH 1	Red	Red	Red	Red	Red
0.05% PCV 0.2% $ZrOCl_2$ pH 1	Red	Red	Red	Blue	Blue
0.05% PCV 1.0% $ZrOCl_2$ pH 1	Red	Red	Red-blue	Blue	Blue

is present to prevent formation of the copper derivative. The colour change is from blue to reddish pink in the presence of arsenate or fluoride. Further experiments where an excess of zirconium was present indicated that some estimate of the amount of arsenate present could be obtained. These results are given in Table V. The fluoride reaction was not further studied, as fluoride containing preservatives are now not extensively used in this country.

CONCLUSIONS

From the foregoing results spot tests using pyrocatechol violet can now be proposed for the detection of preservatives, and the following test solutions are proposed and have been adopted in this laboratory:

Reagent I. 0.1% aqueous solution of Pyrocatechol Violet buffered with 5% ammonium acetate.

Reagent II. 0.05% solution of Pyrocatechol Violet in *N*/10 hydrochloric acid with 0.05% zirconium oxychloride added.

For field testing, where it is merely desired to determine whether the sample is treated with any of the above preservatives, Reagent I will in general be found to be all that is required. As the reagent is not very stable in alkaline solution, it is further recommended that the stock solution of the pyrocatechol violet be made in water and sufficient of the test solution be prepared for each day's testing by the addition of solid ammonium acetate to a portion of the stock solution. The mixed reagent should keep for several days, but the stock solution is stable for many weeks[4]. The information in Tables II and III will then allow any sample to be classed as treated or untreated.

Reagent II will allow the preservative to be classified as containing or not containing arsenic or fluoride, depending on whether the spot becomes pink or remains deep blue.

Where an estimate of the loading is required, this can easily be given using reagent

I with boron-treated wood or by using modified reagents I and II in the case of metal ion- or arsenic-containing wood respectively. No definite composition for these reagents is given, for the desired loading of preservative will vary with the end use of the timber. A series of experiments will, however, quickly give the most satisfactory solution to use for any particular retention of preservative.

In practice, the preservatives listed above, with the exception of boric acid–borax, are usually applied by pressure processes, and salt gradients are not as important as an estimate of completeness of sapwood penetration. Therefore, a clear delineation of the untreated area will satisfy most requirements for testing. This is obtained with either reagent I or II and the modified reagents could well be restricted to laboratory examinations.

The results given above deal with tests carried out using the slightly coloured *P.radiata* wood. The tests have, however, been also applied to the highly coloured indigenous timbers such as rimu, *Dacrydium cupressinum*, and have been found to give good results although blank tests assume the natural colour of the wood. The boron test is especially satisfactory on such timbers as the neutral character of the reagent does not cause the development of the purple colours given by the acid used in the turmeric test and which in many cases effectively masks the test.

ACKNOWLEDGEMENT

The writer is indebted to Mr. A. J. McQuire for the preparation of the test pieces used in this study, to the Director of Forestry for permission to publish.

SUMMARY

The detection of As^{+5}, BO_3^{-3}, Cu^{+2}, Cr^{+3}, Cr^{+6}, Zn^{+2}, and F^- in treated wood with Pyrocatechol Violet is described.

RÉSUMÉ

L'auteur décrit une méthode utilisant le violet de pyrocatéchol pour l'identification de As^{+5}, BO_3^{-3}, Cu^{+2}, Cr^{+3}, Cr^{+6}, Zn^{+2}, F^- dans des bois traités.

ZUSAMMENFASSUNG

Es wird eine Method vorgeschlagen zum Nachweis von As^{+5}, BO_3^{-3}, Cu^{+2}, Cr^{+3}, Cr^{+6}, Zn^{+2}, and F^- in imprägniertem Holz unter Verwendung von Pyrocatechol Violet.

REFERENCES

[1] F. Feigl, *Spot Tests*, 4th English Ed., Vol. I; Elsevier Publishing Company, Amsterdam 1954, p. 416-417.

[2] American wood preservers' association, *Manual of Recommended Practice*, A3-55, July 1957.

[3] W. J. Wilson, *Anal. Chim. Acta*, 19 (1958) 516.

[4] V. Suk and M. Malat, *Chemist-Analyst*, 45 (1956) 4.

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VOLTAMMETRIC, POTENTIOMETRIC AND AMPEROMETRIC STUDIES WITH A ROTATED ALUMINUM WIRE ELECTRODE

II. THE R.Al.E. AS INDICATOR ELECTRODE IN POTENTIOMETRIC AND AMPEROMETRIC ACID-BASE TITRATIONS

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In the first paper of this series[1] it was shown that the rotated aluminum electrode (R.Al.E.) does not function as a pH electrode in acid medium but behaves as a pOH electrode at a pH greater than about 9. Even traces of fluoride ion depolarize the electrode in acid solutions and the electrode potential then becomes considerably more negative than in the absence of fluoride. In order to know the limitations of the R.Al.E. as indicator electrode in potentiometric acid-base titrations in aqueous medium, both in the absence and presence of fluoride in the solution, potential measurements have been made in acid buffer solutions containing varying concentrations of fluoride. Moreover voltammograms were run and measurements of the stationary potential (zero-current potential) of the electrode were made in buffer solutions of various composition in the pH range between 6 and 11, both in the presence and absence of fluoride.

No amperometric titrations of acids with a strong base have been described in the literature. Since hydroxyl ions yield anodic waves at the R.Al.E.[1] with diffusion currents proportional to the concentration of hydroxyl ions, the amperometric titration of strong and intermediate weak acids with standard sodium hydroxide has been studied and the results are reported in the present paper. The end-point could be detected with accuracy and precision even at very low hydroxyl-ion concentrations. The method is very rapid and gives good results even at high dilutions. Examples are given in which the end-point can be detected with much greater accuracy than by classical methods. The limitations of the amperometric titration method are briefly stated.

The experimental technique was the same as that described in the previous paper[1]. Unless otherwise stated, the experiments were carried out in the absence of oxygen.

EXPERIMENTAL RESULTS AND DISCUSSION

Potential measurements and voltammograms in absence of oxygen

Before each measurement the electrode was pretreated in EDTA buffer solution as described previously[1]. The stationary potentials reported in Table I (absence of oxygen) were considered constant when the potential remained unchanged after waiting for another 5 min. The pH of the solutions was determined with the glass electrode after the potential of the R.Al.E. had become constant. The time when this measurement was made had an effect on the pH only in solutions composed mainly of bicarbonate; since nitrogen was swept through or over the solutions, some loss of carbon dioxide occurred continuously.

Although the potential of the R.Al.E. in acid medium is poorly reproducible, the great effect of fluoride on the potential in acid media is clearly recognized in Table I.

TABLE I

EFFECT OF FLUORIDE ON THE POTENTIAL OF THE R.Al.E. IN ACID AND ALKALINE BUFFERS

Electrolyte	*pH*	*NaF concentration M*	$-E$ *vs. S.C.E.*
0.1 *M* $HClO_4$	1.10	$2 \cdot 10^{-5}$	1.231
	1.10	$1 \cdot 10^{-4}$	1.297
	1.15	$1 \cdot 10^{-3}$	1.395
0.01 *M* $HClO_4$	2.10	0	0.6 to 0.8[a]
	2.10	$2 \cdot 10^{-5}$	1.242
	2.10	$1 \cdot 10^{-4}$	1.327
	2.15	$1 \cdot 10^{-3}$	1.432
0.1 *M* HAc + 0.01 *M* $NaClO_4$	2.90	$2 \cdot 10^{-5}$	1.251
	2.95	$1 \cdot 10^{-4}$	1.357
	2.95	$1 \cdot 10^{-3}$	1.456
0.09 *M* HAc + 0.01 *M* NaAc	3.80	$2 \cdot 10^{-5}$	1.269
	3.80	$1 \cdot 10^{-4}$	1.391
	3.80	$1 \cdot 10^{-3}$	1.490
0.05 *M* HAC + 0.05 *M* NaAc	4.60	0	0.7 to 0.9[a]
	4.60	$2 \cdot 10^{-5}$	1.273
	4.60	$1 \cdot 10^{-4}$	1.412
	4.65	$1 \cdot 10^{-3}$	1.505
0.01 *M* HAC + 0.09 *M* NaAc	5.60	0	0.7 to 0.95[a]
	5.60	$2 \cdot 10^{-5}$	1.279
	5.60	$1 \cdot 10^{-4}$	1.427
	5.62	$1 \cdot 10^{-3}$	1.531
0.025 *M* KH_2PO_4 + 0.0028 *N* NaOH	6.00	0	1.0[a]
	6.00	$2 \cdot 10^{-5}$	1.0[a]
	6.00	$1 \cdot 10^{-4}$	1.0[a]
	6.00	$1 \cdot 10^{-3}$	1.3[a]
0.025 *M* KH_2PO_4 + 0.014 *N* NaOH	7.00	$2 \cdot 10^{-5}$	1.05[a]
	7.00	$1 \cdot 10^{-4}$	1.05[a]
	7.00	$1 \cdot 10^{-3}$	1.07[a]
0.025 *M* KH_2PO_4 + 0.0235 *N* NaOH	8.00	$2 \cdot 10^{-5}$	1.06[a]
	8.00	$1 \cdot 10^{-4}$	1.06[a]
	8.00	$1 \cdot 10^{-3}$	1.08[a]
0.028 *M* Veronal + 0.05 *M* NaAc + 0.027 *N* HCl	6.30	0	1.0[a]
	6.30	$2 \cdot 10^{-5}$	1.0[a]
	6.30	$1 \cdot 10^{-4}$	1.1[a]
	6.30	$1 \cdot 10^{-3}$	1.537
0.053 *M* Veronal + 0.046 *N* HCl	7.00	0	1.16[a]
	7.00	$2 \cdot 10^{-5}$	1.17[a]
	7.00	$1 \cdot 10^{-4}$	1.18[a]
	7.00	$1 \cdot 10^{-3}$	1.429

TABLE I (continued)

Electrolyte	*pH*	*NaF concentration M*	*−E vs. S.C.E.*
0.071 *M* Veronal + 0.028 *N* HCl	8.05	0	1.522
	8.05	$2 \cdot 10^{-5}$	1.525
	8.05	$1 \cdot 10^{-4}$	1.527
	8.05	$1 \cdot 10^{-3}$	1.536
0.005 *M* Na_2CO_3 + 0.090 *M* $NaHCO_3$	8.80	$2 \cdot 10^{-5}$	1.578
	8.80	$1 \cdot 10^{-4}$	1.584
	8.90	$1 \cdot 10^{-3}$	1.589
0.05 *M* Borax	9.25	$2 \cdot 10^{-5}$	1.59
	9.25	$1 \cdot 10^{-4}$	1.59
	9.25	$1 \cdot 10^{-3}$	1.60
0.05 *M* Na_2CO_3 + 0.05 *M* $NaHCO_3$	9.85	$2 \cdot 10^{-5}$	1.687
	9.85	$1 \cdot 10^{-4}$	1.690
	9.90	$1 \cdot 10^{-3}$	1.694
0.016 *M* Na_2CO_3 0.004 *M* $NaHCO_3$	10.50	$2 \cdot 10^{-5}$	1.765
	10.50	$1 \cdot 10^{-4}$	1.766
	10.55	$1 \cdot 10^{-3}$	1.769
0.001 *M* Borax + 0.048 *M* Na_2CO_3	10.90	$2 \cdot 10^{-5}$	1.775
	10.95	$1 \cdot 10^{-4}$	1.775
	10.95	$1 \cdot 10^{-3}$	1.777
0.01 *N* NaOH	12.2	0	1.851
	12.2	$2 \cdot 10^{-5}$	1.850
	12.2 (not measured)	$1 \cdot 10^{-3}$	1.855

[a] Potential ill defined; electrode highly polarized.

In alkaline medium (pH > 8) fluoride has no longer an effect on the potential, which is now determined solely by the hydroxyl ion concentration. It is particularly interesting to note that fluoride in phosphate buffers with pH between 6 and 8 does not affect the potential, which is extremely ill-defined. As a matter of fact, in these phosphate buffers fluoride does not depolarize the electrode and does not yield an anodic wave. Some voltammograms in phosphate buffers are shown in Fig. 1. The current-potential curves are practically identical in the pH range between 6 and 9 and they remain unchanged in the presence of fluoride in concentrations as high as 10^{-3} *M*. On the other hand, hydroxyl ions depolarize the electrode in phosphate containing solutions with a pH greater than about 10. Typical examples of this depolarization at pH 10, 10.5 and 11 are illustrated by curves C, D and E in Fig. 1. It should be mentioned that after determining the equilibrium potential in phosphate buffer (pH 6 to 8) the electrode remained polarized in acid buffers containing fluoride. Apparently a film was formed which was not removed by EDTA. Anodic polarization in acid medium in the presence of 10^{-3} *M* fluoride restored the original properties of the electrode.

The observations described for phosphate buffer in the pH range between 6 and 8 do not seem to be specific for phosphate. Similar, but not identical observations have been made in veronal buffers with a pH between 6 and 8. The R.Al.E. remains strongly polarized even when the concentration of fluoride is equal to $1 \cdot 10^{-4}$ *M*. However, in the presence of 10^{-3} *M* fluoride a pronounced anodic depolarization occurs. An example of this effect is given in Fig. 2.

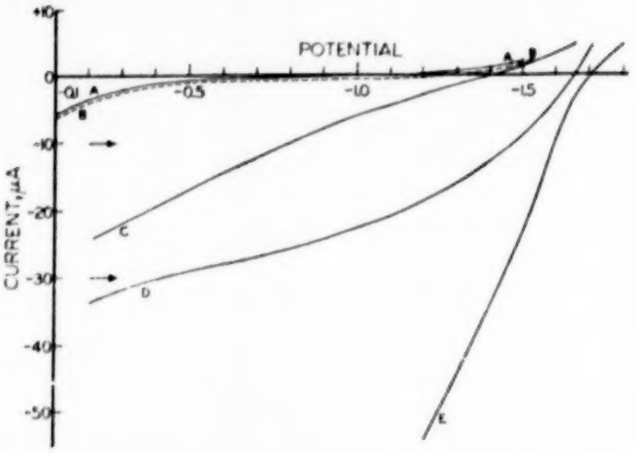

Fig. 1. Voltammograms in phosphate buffers. A, 0.05 *M* KH_2PO_4 + 0.047 *N* NaOH, pH 8.1; B, 0.017 *M* KH_2PO_4 + 0.041 *M* borax, pH 9.0; C, 0.01 *M* Na_2HPO_4 + 0.0004 *N* NaOH, pH 9.9; D, 0.01 *M* Na_2HPO_4 + 0.0012 *N* NaOH, pH 10.5; E, 0.05 *M* Na_2HPO_4 + 0.008 *N* NaOH, pH 11.0.

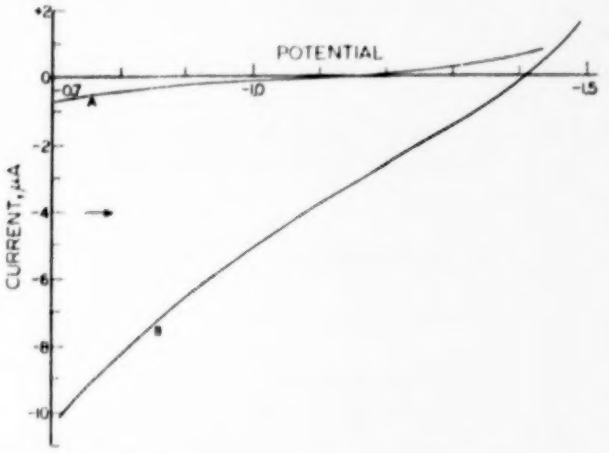

Fig. 2. Voltammograms in 0.053 *M* veronal + 0.046 *N* HCl, pH 7.0. A, $1 \cdot 10^{-4}$ *M* NaF; B, $1 \cdot 10^{-3}$ *M* NaF.

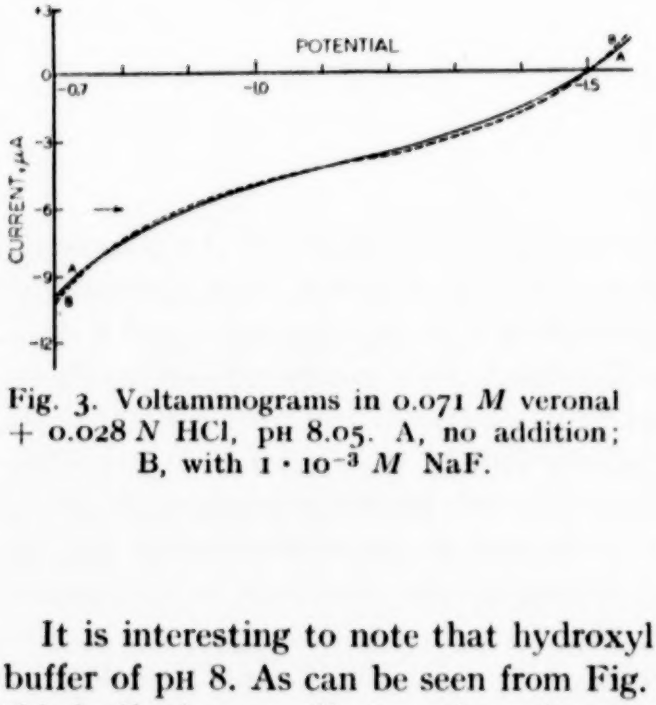

Fig. 3. Voltammograms in 0.071 *M* veronal + 0.028 *N* HCl, pH 8.05. A, no addition; B, with $1 \cdot 10^{-3}$ *M* NaF.

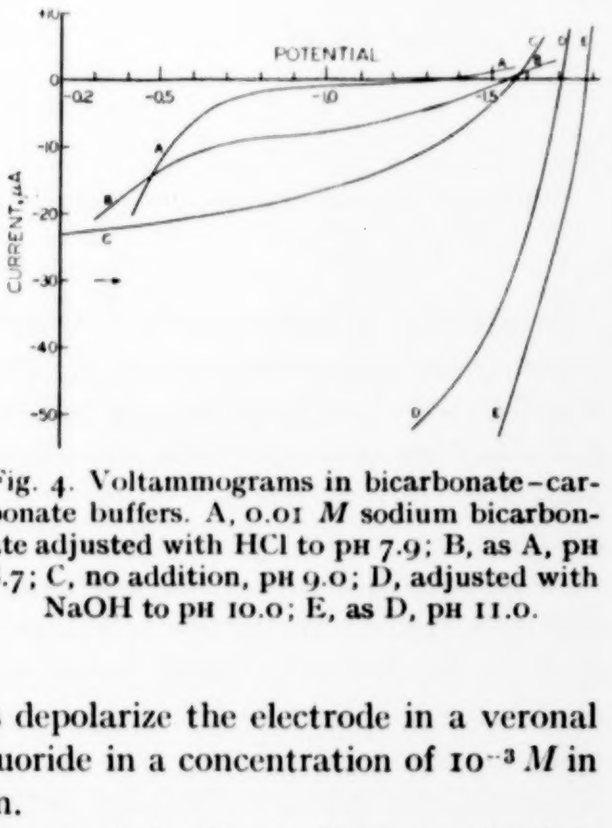

Fig. 4. Voltammograms in bicarbonate–carbonate buffers. A, 0.01 *M* sodium bicarbonate adjusted with HCl to pH 7.9; B, as A, pH 8.7; C, no addition, pH 9.0; D, adjusted with NaOH to pH 10.0; E, as D, pH 11.0.

It is interesting to note that hydroxyl ions depolarize the electrode in a veronal buffer of pH 8. As can be seen from Fig. 3, fluoride in a concentration of 10^{-3} *M* in this buffer has no effect on the voltammogram.

Quite generally, the shapes of voltammograms and also the stationary potentials in the pH range between 8 and 10 vary somewhat with the kind and concentration of the buffer. As an example, some voltammograms in sodium carbonate–bicarbonate buffers are reproduced in Fig. 4. These curves are similar to but not identical with those observed in borate, ammonia–ammonium chloride and veronal buffers of the same pH.

The plot of potential *versus* pH in the presence of various concentrations of fluoride given in Fig. 5 has a very unusual shape. Between pH 1 and 5.5 the potential becomes 30 mV more negative per unit increase in pH at fluoride concentrations between 10^{-3} and 10^{-4} *M*. This value is only 10 mV at a fluoride concentration of $2 \cdot 10^{-5}$ *M*. The potential is extremely badly defined between pH 6 and 8. A continuous line (curve 3 in Fig. 5) is found only in veronal buffers in the presence of 10^{-3} *M* fluoride. In all other instances the potentials are highly irreproducible in the pH range between 6 and 8.

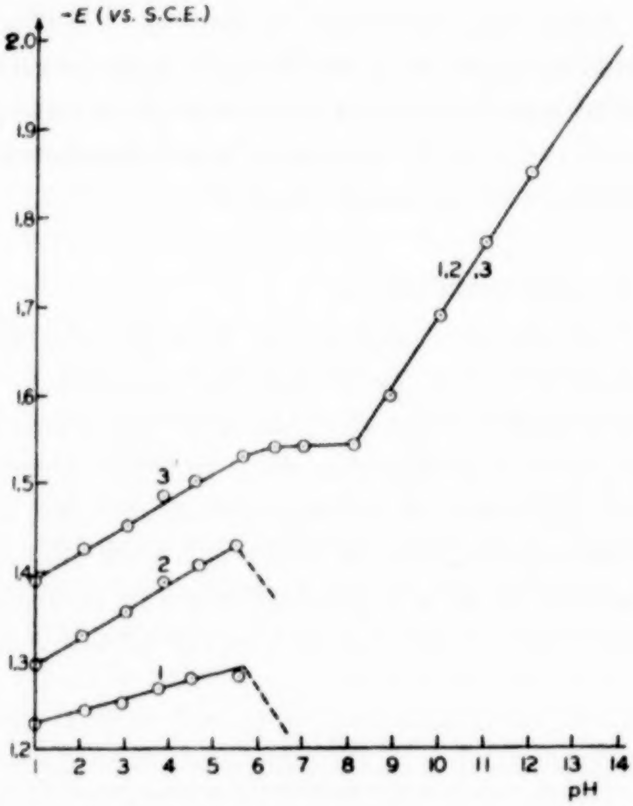

Fig. 5. Potential *versus* pH at various fluoride concentrations. 1, $2 \cdot 10^{-5}$ *M* NaF; 2, $1 \cdot 10^{-4}$ *M* NaF; 3, $1 \cdot 10^{-3}$ *M* NaF.

In phosphate containing solutions the irreproducibility may be observed already at a pH of 5. In such solutions the potential is considerably less negative than may be expected from the curves in Fig. 5. For example, the electrode is strongly polarized in a 0.01 *M* monopotassium dihydrogen phosphate solution of pH 4.95 even in the presence of 10^{-4} *M* fluoride. A fluoride concentration of 10^{-3} *M* is necessary to bring about depolarization and a reproducible potential. This behavior accounts for the unusual titration lines in the titration of a mixture of a strong acid and monopotassium dihydrogen phosphate with a strong base (Fig. 8). At a pH greater than 8 the effect of fluoride on the potential is negligible and a straight line with a slope in the vicinity of 70 mV per unit change in pH is found. The values are in reasonable agreement with those reported previously[1]. In acid medium and at constant pH the electrode potential becomes 100 ± 2 mV more negative when the fluoride concentration is increased from 10^{-4} to 10^{-3} *M*. The depolarization of the aluminum electrode by fluoride may be expected to be given by:

$$\mathrm{Al} + n\mathrm{HF} \rightarrow \mathrm{AlF}_n^{(3-n)+} + n\mathrm{H}^+ + 3e \qquad (1)$$

or

$$\mathrm{Al} + n\mathrm{F}^- \rightarrow \mathrm{AlF}_n^{(3-n)+} + 3e \qquad (2)$$

If these reactions were reversible and if the concentration and also the composition of $\mathrm{AlF}_n^{(3-n)+}$ were constant (slightly soluble), the following expression for the potential at a given pH can be derived:

$$E = \text{Constant} + \frac{RT}{3F} \ln \frac{1}{\Sigma[\mathrm{F}^-]} \qquad (3)$$

in which $\Sigma[\mathrm{F}^-]$ is the total concentration of fluoride ($[\mathrm{HF}] + [\mathrm{F}^-]$). Under these conditions n then would be equal to 5 at fluoride concentrations between 10^{-4} and 10^{-3} *M*. It seems doubtful whether the above assumptions are justified and no further application of equations (1) or (2) is proposed until measurements have been made in solutions in which $[\mathrm{AlF}_n^{(3-n)+}]$ is better defined.

Sensitivity of electrode for traces of fluoride

It has been stated that the potential of the R.Al.E. in acid medium is poorly reproducible. The electrode is highly polarized and potentials vary from day to day probably because of incomplete reproducibility of the surface. Since the potential in acid medium in the absence of fluoride is so poorly reproducible, it is impossible to give an exact figure of the effect of a trace of fluoride upon the potential. However, the data in Table II illustrate that the R.Al.E. is a very sensitive indicator electrode for the detection of fluoride. In an acetate buffer we have always found the potential to be less negative than —1.0 V (*vs.* S.C.E.) in the absence of fluoride. It is fair to state that a potential of —1.05 V in an acetate buffer of pH 3 to 4 definitely indicates the presence of fluoride in the solution. The sensitivity of this test is of the order of $5 \cdot 10^{-6}$ *M* fluoride, corresponding to about 0.1 p.p.m. of fluoride. Since the potential in the fluoride-free acetate buffer depends on the previous history of the electrode, it is recommended that this potential be determined first before measuring the poten-

TABLE II

SENSITIVITY OF THE POTENTIOMETRIC DETECTION OF FLUORIDE

Medium	*pH*	*Fluoride concentration Molar*	*−E vs. S.C.E.*	*Time to attain stationary potential min*
0.1 *M* $\mathrm{HClO_4}$	1.1	0	0,8(0.6–0.8)	∼60
	1.1	$1 \cdot 10^{-6}$	0.85	35
	1.1	$1 \cdot 10^{-5}$	1.17	35
	1.1	$2 \cdot 10^{-5}$	1.23	15
0.09 *M* HAc + 0.01 *M* NaAc	3.8	0	0.8–1.0	∼60
	3.8	$1 \cdot 10^{-6}$	1.06	40
	3.8	$1 \cdot 10^{-5}$	1.20	25
	3.8	$2 \cdot 10^{-5}$	1.27	15
		$2 \cdot 10^{-5}$	1.26[a]	
		$2 \cdot 10^{-5}$	1.24[b]	

[a] In presence of 0.01 *M* $\mathrm{Na_2SO_4}$
[b] In presence of 0.01 *M* $\mathrm{KH_2PO_4}$

tial of the unknown. The test is highly selective and is not interfered with by moderate concentrations of sulfate, phosphate and other common ions. We have applied the test to the detection of fluoride in six different potable water species and were able to detect 0.2 p.p.m. of fluoride with certainty. The test must be carried out in the absence of oxygen. Other oxidizing agents (copper, silver ions, permanganate) make the electrode potential less negative and must be removed.

Effect of oxygen on the fluoride potential and on the anodic waves at the R.Al.E. in acid media

In the first paper of this series it was stated that oxygen does not affect the poorly reproducible potential of the R.Al.E. in acid medium. There is no indication of cathodic depolarization of the electrode by oxygen. However, the situation is entirely different in the presence of fluoride. Voltammograms and potentials were determined in 0.1 and 0.01 *M* perchloric acid and in acetate buffers with a pH varying between 3.2 and 4.6, all solutions being 10^{-4} *M* in fluoride and either saturated with oxygen or made oxygen-free with the aid of pure nitrogen. After the stationary potential in the nitrogen saturated solution had been established, a current-potential curve was run from positive to negative potentials. The solution was then saturated with oxygen and the procedure repeated. Qualitatively, the effect of oxygen was the same in all solutions; oxygen shifts the anodic wave and the potential to less negative values (Table III), and in some instances the diffusion current of fluoride is not attained in the oxygen saturated solutions. An illustration of this effect is given in Fig. 6; some quantitative data on the magnitude of the shift of the "fluoride potential" by oxygen are reported on Table III. The effect of oxygen on the potential is considerably smaller at a pH of 1 than it is in less acid solutions (pH 3.8 and 4.6). The presence of fluoride in the solution appears to facilitate the reduction of oxygen at the R.Al.E.

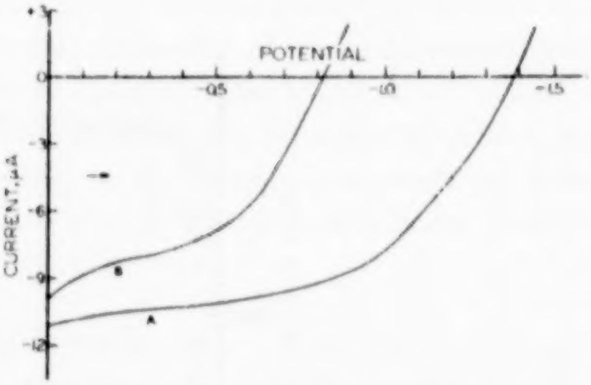

Fig. 6. Voltammograms of fluoride in presence and absence of oxygen; $1 \cdot 10^{-4}$ *M* NaF in 0.09 *M* HAc + 0.01 *M* NaAc, pH 3.8. A, saturated with nitrogen; B, saturated with oxygen.

TABLE III

EFFECT OF OXYGEN ON THE POTENTIAL (E) OF THE R.Al.E. IN 10^{-4} *M* FLUORIDE SOLUTION

Electrolyte	*pH*	$-E_{N_2}$ *vs. S.C.E.*	$-E_{O_2}$ *vs. S.C.E.*	ΔE *V*
0.1 *M* $HClO_4$	1.1	1.295	1.081	0.214
0.09 *M* HAc + 0.01 *M* NaAc	3.8	1.387	0.822	0.565
0.05 *M* HAc + 0.05 *M* NaAc	4.6	1.405	0.891	0.514

The potentials measured in the presence of oxygen are therefore typical "mixed potentials"[2]. At such a potential the anodic fluoride current is equal to the cathodic oxygen current. For example, in Fig. 6 the fluoride current in a nitrogen atmosphere at a potential of —0.82 V is approximately 9 μA, but in an oxygen-saturated solution it is apparently equal to zero. Actually, in the latter solution the anodic fluoride current would be expected to be 9 μA while it is compensated by an oxygen reduction current of equal magnitude. Other examples of mixed potentials at an aluminum electrode in ceric sulfate in acid medium and in ferricyanide in acid and alkaline media have been reported by PETROCELLI[3,4].

Potentiometric acid–base titrations

In the preceding sections and the previous paper[1] it has been stated that the potential of the R.Al.E. is not well defined in acid medium and that the electrode does not function as a pH electrode until the hydroxyl-ion concentration is about 10^{-6} *M* or greater. During a potentiometric titration of an acid with a strong base the potential was found to vary very little in the pH range between 1 and 8, but it becomes very much more negative when the pH increases further. Use of this fact has been made by SCARANO[5] who has described acid–base titrations using aluminum as an indicator electrode.

Curve A in Fig. 7 represents the titration curve of 50 ml of 0.01 *N* hydrochloric acid with 0.127 *N* standard carbonate-free sodium hydroxide. In the immediate vicinity of the end-point, a large break in potential from about —0.95 to —1.6 V is observed. The potentiometric end-point (first and second derivatives) could be determined with an accuracy and precision of 0.2%. As could be expected, the break in potential becomes considerably less pronounced in the presence of a trace of fluoride (see Table I and curve B in Fig. 7). Practical advantages of adding a trace of fluoride to the so-

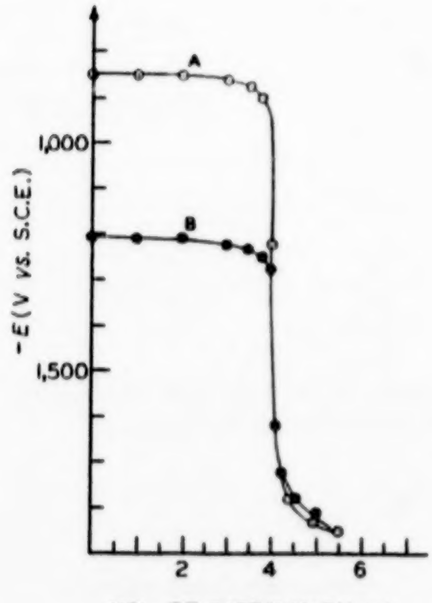

Fig. 7. Titration curves of 0.01 *N* HCl with 0.127 *N* NaOH. A, absence of fluoride; B, $2 \cdot 10^{-5} M$ NaF added. Calculated stoichiometric end-point 3.997 ml; found: 3.990 ml.

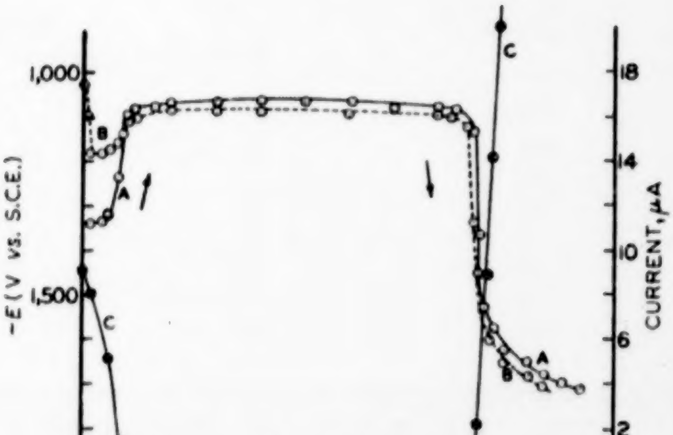

Fig. 8. Potentiometric and amperometric titration curves of a mixture of 0.001 *N* HCl + 0.01 *M* KH_2PO_4, in the presence and absence of $1 \cdot 10^{-4} M$ NaF. Applied potential in the amperometric titration: —1.0 V (*vs.* S.C.E.). A, potentiometric curve in the presence of $1 \cdot 10^{-4} M$ NaF; B, same as A, in the absence of fluoride (dotted line); C, amperometric curve in presence of $1 \cdot 10^{-4} M$ NaF.

lution to be titrated, are that the potential becomes well defined in acid medium and that it takes much less time to attain its constant value at a pH smaller than 8. Even 0.001 *N* hydrochloric acid could be titrated (absence of fluoride) with an accuracy and precision of 2%. Similarly, 0.001 *N* solutions of acetic acid and of potassium biphthalate were titrated with the same accuracy in the absence or presence of fluoride. In the absence of fluoride these titrations are much less time consuming if standard base is added until an "end-point potential" of —1.20 V is attained. This potential corresponds to an end-point pH of about 8. A very interesting plot (Fig. 8) is observed in the titration of a mixture of a strong acid and monopotassium dihydrogen phosphate containing a trace of fluoride, with sodium hydroxide. In such a mixture two potential breaks are obtained (curve A in Fig. 8). The first end-point, corresponding to the neutralization of the strong acid, is indicated by a potential break in the "wrong" direction (from negative to more positive potentials). The potential hardly changes during the neutralization of the free strong acid in the presence of fluoride. Immediately after neutralization of the strong acid the electrode becomes highly polarized, even though fluoride is present (see Table I) and the potential becomes some 250 mV less negative. The potential then hardly changes during the neutralization of dihydrogen phosphate to monohydrogen phosphate until very close to the end-point (pH around 8) when the electrode becomes depolarized by hydroxyl ions. A large break in potential of the order of 500 mV is observed at the end-point. The first end-point was found after addition of 0.41 ml 0.127 *N* standard base (calculated 0.40 ml) and the second end-point after addition of 4.43 ml (calculated 4.40 ml). It is evident from Fig. 8 that in the absence of fluoride the first end-point is made less pronounced by the polarization of the electrode by the phosphate. The second end-point corresponding to monohydrogen phosphate is found at the right location either in the absence or presence of fluoride, which substantiates the conclusion that fluoride in alkaline medium has practically no effect upon the potential.

It is hardly to be expected that the R.Al.E. will find much application in acid–base titrations in aqueous media, since the glass electrode and other pH indicating electrodes respond much more quickly and yield much more reliable data of the pH during a titration. For this reason, the limitations of the R.Al.E. in potentiometric acid–base titrations will not be discussed. It is possible, however, that the electrode may find wider application in non-aqueous titrations. It is planned to study the use of the electrode under such conditions.

Amperometric acid–base titrations

As has been shown in the first paper of this series[1] hydroxyl ions depolarize the aluminum electrode yielding an anodic wave with a well defined diffusion current at —1.0 V *vs.* S.C.E. Thus, it may be expected that strong and weak acids with a dissociation constant greater than about 10^{-8} can be titrated amperometrically with a strong base. The titration can be carried out very rapidly, even in very dilute solutions. For example, the amperometric titration of 0.001 *N* hydrochloric acid with 0.1 *N* carbonate-free standard sodium hydroxide at —1.0 V (S.C.E.) gave results which were accurate and precise to within 2%. Similar results were obtained in the titration of 0.001 *N* acetic acid and biphthalate. As an illustration, the amperometric titration curve of 0.001 *M* potassium biphthalate is given in Fig. 9. The right hand side ordinate gives the values of the diffusion current of free hydroxyl ions after the end-point. For comparison the potentiometric titration curve is also plotted. In the amperometric titration of 0.00025 *N* biphthalate the end-point was found with an accuracy of 5%.

The titration of a mixture of 0.001 *N* hydrochloric acid and 0.01 *M* monopotassium phosphate in the presence of 10^{-4} *M* fluoride can also be followed amperometrically, and the titration lines are shown in Fig. 8. In the presence of free acid an anodic fluoride current is measured at —0.1 V. This current is less than the diffusion current since the phosphate starts to interfere at a pH around 4. At a pH of about 5.5 the electrode becomes completely polarized by the phosphate and the anodic current becomes zero. The titration line (curve C in Fig. 8) is not straight but curved. The extrapolated end-point gives about 20% high value for the neutralization of the strong acid.

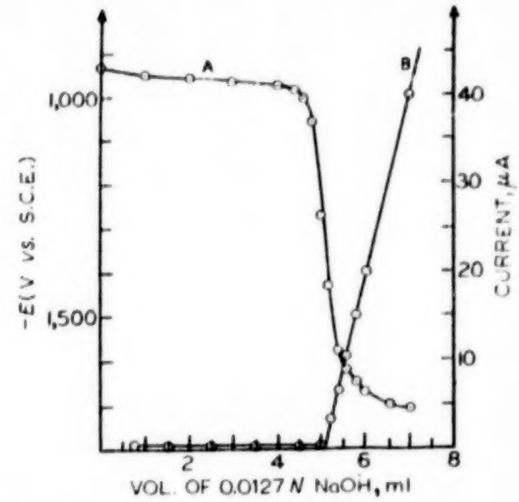

Fig. 9. Potentiometric and amperometric titration curves of 0.00127 *M* potassium biphthalate; applied potential in the amperometric titration: —1.0 V (*vs.* S.C.E.). A, potentiometric curve, end-point, 4.95 ml; B, amperometric curve, end-point, 5.05. Calculated end-point: 5.00 ml.

After complete neutralization of the dihydrogen phosphate to monohydrogenphosphate an anodic current is measured again. This current is caused by hydroxyl ions and it increases with excess of base (curve C in Fig. 8). The second end-point was found after addition of 4.41 ml of standard base (calculated 4.40 ml).

ACKNOWLEDGEMENT

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SUMMARY

The effect of varying concentrations of fluoride on the potential of the R.Al.E. in acid buffer solutions is reported. In the pH range between 1 and 5.5 the potential becomes 30 mV more negative per unit increase in pH at fluoride concentrations between 10^{-3} and 10^{-4} *M*. At a given pH the potential becomes 100 mV more negative when the fluoride concentration is increased from 10^{-4} to 10^{-3} *M*. No depolarization occurs and no reproducible potentials can be measured in phosphate buffers of pH 6 to 8, even in the presence of 10^{-3} *M* fluoride. This concentration of fluoride causes depolarization and establishment of reproducible potentials in veronal buffers of reproducible pH 6 to 8. At a pH greater than 9 fluoride has no effect on the electrode potential which now becomes determined by pH. In the presence of fluoride, oxygen shifts the electrode potential to less negative values (mixed potential). Examples of potentiometric and amperometric titrations of strong and weak acids are given with the R.Al.E. as indicator electrode.

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RÉSUMÉ

Les auteurs ont étudié l'influence de concentrations variables de fluorure sur le potentiel d'une électrode tournante d'aluminium, dans des solutions tampon acides à divers pH. Des exemples de titrages potentiométriques et ampérométriques au moyen de l'électrode tournante d'aluminium sont donnés pour des acides forts et des acides faibles.

ZUSAMMENFASSUNG

Es wurde der Einfluss wechselnder Fluorid Konzentrationen auf das Potential einer rotierenden Aluminiumelektrode in sauren Pufferlösungen bei verschiedenem pH untersucht. Beispiele für potentiometrische und ampérometrische Titrationen starker und schwacher Säuren mit Hilfe der rotierenden Aluminiumelektrode werden angeführt.

REFERENCES

[1] I. M. Kolthoff and C. J. Sambucetti, *Anal. Chim. Acta*, 21 (1959) 17.
[2] I. M. Kolthoff and C. S. Miller, *J. Am. Chem. Soc.*, 62 (1940) 2171.
[3] J. V. Petrocelli, *J. Electrochem. Soc.*, 97 (1950) 10.
[4] J. V. Petrocelli, *J. Electrochem. Soc.*, 99 (1952) 513.
[5] E. Scarano, *Anal. Chim. Acta*, 16 (1957) 365.

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DETERMINATION OF MAGNESIUM IN NODULAR CAST IRON, USING A CHROMATOGRAPHIC SEPARATION

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INTRODUCTION

Trends in recent chemical methods for the determination of magnesium in cast iron have been towards simplified separation techniques, enabling results to be obtained quickly. This is shown by a comparison of the methods of Green[1], Zindel[2] and Reichert[3] with those of Westwood and Presser[4], Yarne and Sobers[5] and the A.S.T.M.[6] Shiokawa and Sato[7] have successfully used an ion-exchange resin for the separation of small amounts of boron and magnesium from large quantities of iron. Apart from this work, chromatographic methods, which are simple and require little manipulation, do not appear to have received much attention. This prompted the author to investigate the possibilities of cellulose column chromatography, which has been used in the determination of other constituents of iron and steel[8-10]. A procedure taking about 4 h was developed, utilizing a volumetric finish (with EDTA) after the initial separation from interfering elements.

EXPERIMENTAL

Reagents

Solvent: Methyl ethyl ketone, reagent grade.

Elution mixture: Methyl ethyl ketone 98 ml
10 *N* Hydrochloric acid 2 ml } freshly prepared.

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* This work was undertaken in part fulfilment of the requirements for an Honours B.Sc. degree at the N.S.W. University of Technology, Sydney (Australia).

EDTA: Disodium salt (reagent grade) 3.7 g/l.
Indicator: 1% Eriochrome Black in equal parts of ethanol and triethanolamine.
Buffer solution: Ammonium chloride 6.75 g, 15 N Ammonia 57 ml } per 100 ml
Ascorbic acid: Reagent grade.

Preliminary experiments

The elution mixture was chosen on the basis of tests with a synthetic cation mixture, chromatographed on paper strips (ascending solvent). Iron was readily separated from magnesium and manganese which remained at R_F 0–0.1. Further tests with cellulose columns indicated that magnesium was retained in the column until all iron and manganese had been eluted.

Column preparation

A uniform column about 9 cm long in a silicone-treated glass tube, 1.3 cm in diameter, was prepared from a slurry of Whatman's standard grade cellulose for chromatographic purposes. (5 g in 50 ml of N hydrochloric acid). The column was conditioned by washing successively with 50 ml of N hydrochloric acid, 150 ml of distilled water, 50 ml of solvent and 100 ml of elution mixture.

Procedure

1 g of iron was dissolved in 30 ml of 5 N hydrochloric acid; the hot solution was oxidised with 5 ml of 15 N nitric acid, then evaporated to dryness and baked for 5 min at about 200°. The residue was warmed with 15 ml of 10 N hydrochloric acid until the salts were dissolved; 25 ml of distilled water was added and the solution was heated to near boiling, then filtered. The residue was washed with hydrochloric acid and hot water, and the filtrate was evaporated just dry; the salts were re-dissolved in 4 ml of 10 N hydrochloric acid, with gentle warming. To the cooled solution, 10 ml of elution mixture was added; the mixture was swirled thoroughly, then poured onto the column. The beaker was rinsed with 2-ml portions of elution mixture. Two phases resulted, the lower layer being light yellow-brown in colour. Gentle suction was applied till the liquid level was just above the top of the column. The tube walls were washed with small portions of elution mixture, draining (without letting the top of the column become dry) between rinses. Finally, the tube was filled with elution mixture, and elution was continued at 1–2 ml/min until a total of 100 ml had passed through the column; the eluate was discarded. 80 ml of 1% hydrochloric acid was then passed through the column to recover the remaining metals. To this extract, 1 g of ammonium chloride was added, and the solution was made ammoniacal with 2 ml of 5 N ammonia in excess; the solution was heated to boiling, then 2 ml of 10% ammonium oxalate was added dropwise. The flocculated precipitate was filtered off and washed twice with distilled water; to the filtrate, 10 ml of 10% potassium cyanide, 4 ml of buffer solution and 1 g of ascorbic acid were added, and the volume was adjusted to 150 ml with distilled water. Four drops of indicator were added, and the magnesium was titrated with EDTA to a clear blue end-point. The end-point colour change was not as sharp as desired, so the EDTA was standardized (against pure magnesium sulphate) under the same lighting conditions, and wit the same reagents present in solution. Pyrocatechol Violet, introduced by SUK

et al.[11], was tried as an alternative indicator, but was considered inferior to Eriochrome Black in this case.

Separations achieved in the column

Spectrographic examination of various fractions collected from the column in a number of runs, showed that during solvent elution:

(a) In a few cases, small amounts of magnesium were found in the eluate (60–100 ml); in most cases, negligible amounts of magnesium passed out of the column.
(b) Vanadium, titanium, and chromium were completely retained in the column.
(c) Aluminium and nickel were retained almost completely in the cellulose; small amounts passed out in the 60–100 ml fraction.
(d) Calcium was distributed between the eluate and the column.
(e) Iron and manganese were completely removed from the column.

Notes on stages observed during solvent elution

A bright yellow-brown layer separated out on transfer of the sample to the tube; as this band passed through the column, it was followed by a greenish-yellow zone; under ideal conditions, the solvent front appeared as a sharp line.

The bulk of the iron was removed with the first 40 ml of solvent; a thin blue-green zone, rich in manganese, followed the iron, and was usually removed when 70 ml of solvent had passed through the column. With samples containing nickel, chromium, titanium and vanadium, the eluted column had a pale brownish-yellow tint, more marked towards the top.

Marked changes in filtration rate were noted; while the main acid-rich fraction was being eluted, the rate dropped considerably; as the iron passed out of the column, the rate increased sharply; on elution with dilute acid, the filtration rate slowed up again.

Removal of interfering ions before titration of magnesium

Spectrographic tests showed that there was no loss of magnesium in the ammonia precipitation step; the solution for titration contained only magnesium and nickel, with faint traces of calcium and aluminium.

RESULTS

Standards

Standard iron samples of known magnesium content were not available. Standards were made by additions of magnesium to solutions of pure iron (Adam Hilger Ltd. Analysis: Mg 0.001%, Mn 0.1 p.p.m., Ni 0.0035%, Co 0.003%, Ca Nil).

Blank tests were carried out on the pure iron and on the reagents. Results are shown in Table I.

TABLE I

RECOVERY OF MAGNESIUM FROM SYNTHETIC STANDARDS

Magnesium added mg	*Magnesium found* mg	*Recovery* %
Nil	Nil	—
1.10	1.10	100
0.55	0.56	102
0.55	0.55	100

TABLE II

ANALYSIS OF CAST IRON BY THE CHROMATOGRAPHIC SEPARATION METHOD

Sample	Magnesium found %			Mean %	Standard deviation %
1	0.026	0.027	0.028	0.029	7.9
	0.028	0.031	0.032		
2	0.030	0.033	0.038	0.035	11.4
		0.039			
3	0.034	0.035	0.038	0.038	10.8
	0.042	0.043			
4	0.055	0.053		0.054	—
5	0.052	0.055	0.060	0.058	9.1
		0.064			
6	0.060	0.068	0.074	0.070	11.3
		0.078			

Analysis of nodular cast iron

Six samples were examined by the new method and by other comparable rapid methods. The results are set out in the Tables II and III.

TABLE III

COMPARISON OF DIFFERENT METHODS FOR DETERMINATION OF MAGNESIUM

Method	% Mg found in sample					
	1	2	3	4	5	6
Chromatographic	0.029	0.035	0.038	0.054	0.058	0.070
Spectrographic	0.032	0.038	0.032	0.051	0.055	0.063
GREEN's method (single determination only)	—	0.044	0.041	0.064	0.058	0.058
REICHERT's method	— See Notes —					

Notes on Table III

1. Spectrographic analyses were made by a newly developed method[12], using a Hilger 3-metre grating spectrograph, and sparking solutions of iron on copper electrodes. Standards were prepared from pure iron rod and pure magnesium sulphate. The standard deviation of replicate analyses was approximately 5%.

2. GREEN's non-stoichiometric zinc oxide–ammonium persulphate separation method[1] was followed; the magnesium was titrated directly with EDTA, and no Tiron was added.

3. REICHERT's method[3] using a single precipitation with ammonia and hydrogen sulphide to remove interfering metals before titration of magnesium with EDTA, was tried; satisfactory results were not obtained, as considerable quantities of magnesium appeared to be retained in the voluminous sulphide precipitate.

DISCUSSION

Chromatographic separation procedures are largely empirical, because of the interdependence of various parameters such as filtration rate, acidity gradients, maintenance of solvent equilibrium and complex formation. For efficient column operation, care in the packing and conditioning steps is essential; filtration rate should be controlled, since too rapid a flow causes considerable "tailing off" of the iron zone.

Because standard samples of known magnesium content were not available, the accuracy of the method was not fully checked in this work, but in view of the good results with the synthetic standards, and the fair agreement with the spectrographic

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work, it was considered that the method, although not highly reproducible, (± 10%), might be acceptable for routine work, since results can be obtained quickly, with simple apparatus. Care in sampling test blocks is necessary, as YARNE AND SOBERS[5] have shown that marked segregation of magnesium can occur.

The observed quantitative retention of titanium, chromium and vanadium in the column suggests further useful applications for the separation of traces of these elements.

ACKNOWLEDGEMENTS

I wish to thank my tutor Mr. E. C. MARTIN, of the N.S.W. University of Technology, for his encouragement and assistance; Mr. L. RANNIT of the above University, who carried out all the spectrographic work; the N.S.W. Government Railways Testing Laboratories, and Mr. FORBES SMITH of Howard Autocultivators Pty. Ltd., who so kindly supplied test samples.

SUMMARY

Small amounts of magnesium present in solutions of cast iron can be separated by partition chromatography on cellulose columns. Magnesium may then be determined volumetrically. The method is rapid and gives results which appear acceptable for routine work. No elaborate apparatus is required.

RÉSUMÉ

Une méthode rapide est proposée pour le dosage de petites quantités de magnésium dans une fonte. On effectue une séparation par chromatographie de partage sur colonnes de cellulose et on dose ensuite le magnésium par volumétrie.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Schnellbestimmung von Magnesium in Gusseisen. Die Abtrennung des Magnesiums erfolgt nach dem Prinzip der Verteilungschromatographie mit einer Cellulosekolonne. Das eluierte Magnesium wird anschliessend volumetrisch bestimmt.

REFERENCES

[1] H. GREEN, *Brit. Cast Iron Research Assoc., J. Research and Develop.*, 6 (1955) 20.
[2] E. ZINDEL, *Giesserei Techn. Wiss. Beih. Giessereiw. u. Metallk*, 14 (1956) 869. (*Chem. Abstr.*, 51 (1957) 4209 b).
[3] R. REICHERT, *Giesserei*, 44 (1957) 51; (*Chem. Abstr.*, 51 (1957) 6431 e).
[4] W. WESTWOOD AND R. PRESSER, *Brit. Cast Iron Research Assoc., J. Research and Develop.*, 3 (1950) 515. (Research Report No. 264).
[5] Y. L. YARNE AND W. B. SOBERS, *Am. Foundryman*, 17 (1950) 33.
[6] A.S.T.M., *Methods of Chemical Analysis of Metals*, 1956, E30-56T.
[7] TAKANOBU SHIOKAWA AND AKIKO SATO, *Nippon Kinzoku Gakkai-Shi*, B15, (1951) 284. (*Chem. Abstr.*, 47 (1953) 8578 b).
[8] F. H. BURSTALL, G. R. DAVIES AND R. A. WELLS, *Discussions Faraday Soc.*, 7 (1949) 179.
[9] J. R. BISHOP, *Analyst*, 81 (1956) 291.
[10] G. VENTURELLO AND A. M. GHE, *Analyst*, 82 (1957) 343.
[11] M. MALÁT, V. SUK AND A. JENÍČKOVÁ, *Collection Czechoslov. Chem. Communs.*, 19 (1954) 1156. (*Chem. Abstr.*, 49 (1955) 6768 h).
[12] L. RANNIT, *N.S.W. University of Technology, Sydney (Australia)*; unpublished work.

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FACTORS AFFECTING THE ULTRAMICRO-DETERMINATION OF TRYPTOPHAN, KYNURENINE AND THEIR DERIVATIVES

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INTRODUCTION

In order to study the metabolic breakdown pathways of tryptophan, a technique is needed which can be adapted to the resolution of the by-products and to their quantitative determination. Paper chromatography and paper electrophoresis were investigated for possible use.

Fluorospectrophotometric methods have been investigated[1] in the microdetermination of certain fluorescing compounds, *i.e.*, tryptophan, kynurenine, anthranylic acid, etc., — in biological extracts and known solutions. These procedures are available when individual compounds are known to be present, but the presence of interfering compounds such as tryptophan derivatives or breakdown products limits their use and resolution is required before quantitative spectrophotometric analysis. The present investigation reports on the resolution and quantitative estimation of tryptophan and kynurenine from paper electrophoresis and paper chromatography.

The results obtained indicate that the electrolyte used in electrophoresis influences the mobility, the separation and the ultraviolet spectra of tryptophan and kynurenine. The pre-treatment of filter paper (see below) did not influence the R_F of tryptophan and kynurenine, but affected their quantitative determination. Elution of tryptophan or kynurenine from chromatograms or electrograms varied with the type of pH of the eluant. Unexpected interaction of kynurenine with certain electrolytes (phosphate, and borate buffers used in electrophoresis) resulted in the appearance of at least two kynurenine derivates.

Ultraviolet irradiation of either *l*- or *d*-tryptophan in aqueous solutions results in changes of their characteristic ultraviolet spectrum, and electrophoretic mobility. The pH of the solutions decreases and the solutions become colored with a faint odor.

EXPERIMENTAL

Materials

Whatman filter paper No. 1 was used. Three types of this filter were prepared: unwashed (as supplied by the manufacturer (A), washed with distilled water (B) and washed with 0.05*N* HCl (C). The amino acids *l*-tryptophan, *d*-tryptophan, *dl*-tryptophan, *l*-kynurenine, *d*-kynurenine and *dl*-kynurenine were all of the c.p. grade obtained from Mann Research Laboratories, and were purified so as to obtain chromatographically pure material. The optical rotation of each was checked before every experiment. All alcohols used were freshly distilled.

Chromatography

Tryptophan or kynurenine isomers were separated by paper chromatography. The solvent used consisted of equal volumes of 95 % ethanol and 0.1*N* acetic acid. The compounds were located by examining the chromatograms under ultraviolet light. Tryptophans gave purple fluorescence, while kynurenines gave orange fluorescence when the dried chromatograms were examinated without further treatment. After spraying the paper with 1*M* KCN, drying and re-examining under ultraviolet light, both tryptophan and kynurenine remained visible. After exposure to KCN, drying and spraying with Ehrlich reagent, tryptophan and kynurenine each produced a characteristic color.

Chromatograms sprayed with ninhydrin or Ehrlich reagent were used to locate tryptophan or kynurenine on unstained chromatograms. From duplicate untreated chromatograms, triangular wedges containing the located amino acids were cut out. The material was concentrated at the pointed tip of the wedge by dipping the broad side of the triangle in distilled water[2]. After concentration, the pointed end of each wedge was cut and carefully placed on an already equilibrated paper electrophoresis apparatus.

Paper electrophoresis

Electrophoresis was performed in a type LKB 3276 electrophoresis apparatus, using 40 × 4.0 Schleicher and Schull No. 2043B filter paper, or in an electrophoresis apparatus as described earlier[3]. The following buffer systems were used: 0.2*M* phosphate buffers from pH 5.288–pH 8.043; 0.1*M* acetate buffers from pH 3.820–pH 5.120, and 0.01*M* borate buffer, pH 8.5. An average of 300 V potential and 0.05 mA current was used for a period of 10 h.

Ultraviolet spectrophotometric analysis

Compounds located on sprayed chromatograms were cut from duplicate untreated chromatograms and eluted in sterile distilled water, 0.05*N* HCl or NaOH–$NaHCO_3$.

RESULTS

Tryptophan and kynurenine were resolved by paper chromatography and paper electrophoresis, eluted and quantitatively determined. The behavior of tryptophan in paper chromatography was found to be influenced by the type or conditioning of the paper. Three types of filter paper were used: (A, B, C, as above). Although on these three papers, tryptophan showed comparable R_F position and fluorescence, when examined under ultraviolet light, elution data and ultraviolet spectra were variable.

Washing the filter paper with distilled water altered it porosity and its tissue structure in such a way as to reduce the recovery of tryptophan in distilled water. Only 51% of tryptophan was recovered from paper B, while from A or C papers, 88 and 83% recovery was obtained respectively. In acidic eluants (0.05*N* HCl) tryptophan was recovered to the extent of 81, 76 and 83% from filter papers A, B and C. Using alkaline eluants (NaOH, $NaHCO_3$) 84 to 86% of tryptophan was recovered from the three types of filter paper.

Tryptophan, on paper electrophoresis, using neutral (phosphate buffer), alkaline (borate buffer), or acid (acetate buffer) moved as one component. The relative electromobility of tryptophan in the above three buffers was 1 : 7 : 7 in borate, phosphate and acetate respectively. Elution data showed variations (71 to 93%) in recovery, depending on the buffer used in electrophoresis and the eluant. The best conditions for tryptophan recovery were as follows: from papers in phosphate buffer, 86% was recoverd using 0.05*N* HCl as the eluant; from papers in borate or acetate buffers, 91 and 93% recovery were obtained respectively with NaOH–$NaHCO_3$ as the eluant.

Spectrophotometric analysis of tryptophan studied at wave lengths of 220–330 mμ showed slight variations between the maximum and the minimum of the spectral curve. Fig. 1 presents the ultraviolet spectra of tryptophan in distilled water, in 0.05*N* HCl and in 0.05*N* NaOH. The tryptophan spectrum in 0.05*N* H_2SO_4 resembles the spectrum in HCl, and the spectrum of tryptophan in NaOH–$NaHCO_3$ shows a certain resemblance to that in NaOH. Variations in ratios (minimum : maximum) and in the rate of change of the spectral curve ($O.D._{min}$—$O.D._{max}$) are presented in Fig. 2. It is evident from the data presented that quantitative spectrophotometric determinations of tryptophan vary with the pH, ionic concentration and type of buffer used. Our data indicates that the smalles quantitative error is obtained in carrying out spectrophotometric determinations at pH 5.0–6.0.

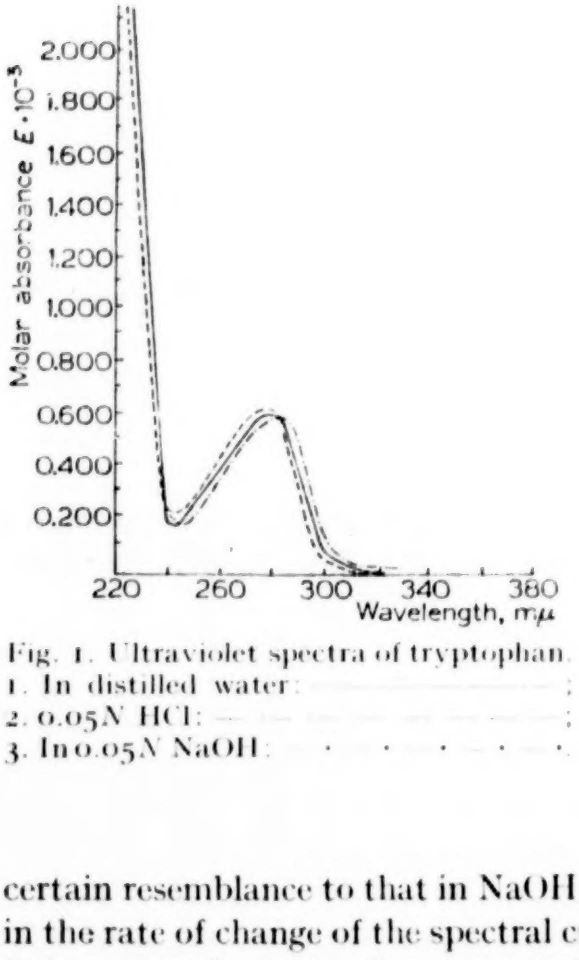


Fig. 1. Ultraviolet spectra of tryptophan. 1. In distilled water: ———; 2. 0.05*N* HCl: — — — —; 3. In 0.05*N* NaOH: · · · · · ·.

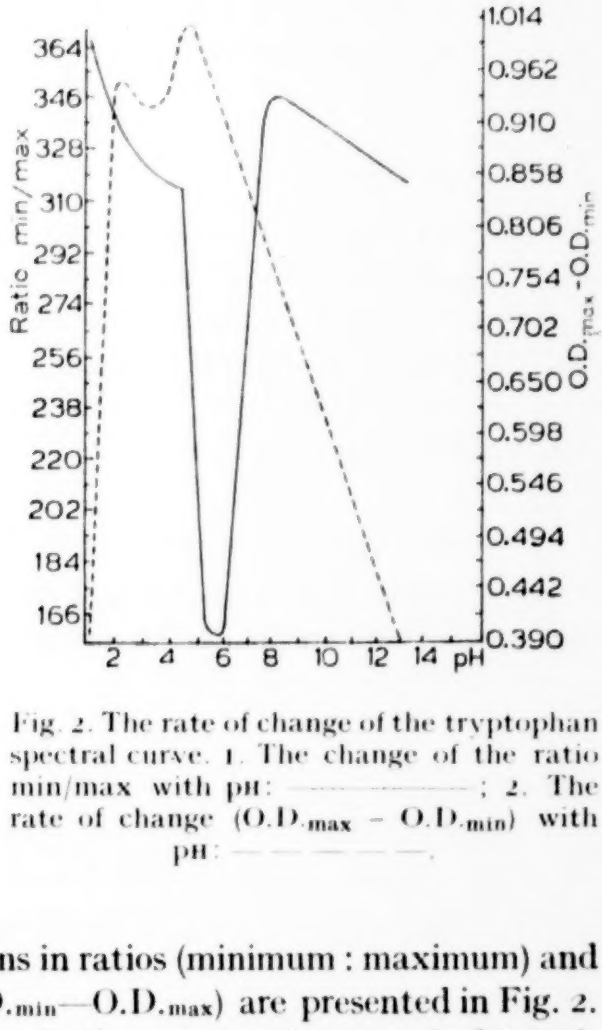


Fig. 2. The rate of change of the tryptophan spectral curve. 1. The change of the ratio min/max with pH: ———; 2. The rate of change ($O.D._{max}$ − $O.D._{min}$) with pH: — — — —.

Similar to tryptophan, kynurenine was found to be influenced by the conditioning of the filter paper for chromatography and by the buffer used for electrophoresis. On paper chromatography *dl*-kynurenine was resolved into *d* and *l* with ethanol–acetic acid and water solvent. The recovery of total kynurenine (*d* and *l*) was found to be 97, 87 and 87%, from (A), (B) and (C) papers respectively, using 0.05*N* HCl, distilled water or NaOH–$NaHCO_3$ as an eluant; much lower recovery percentages were obtained when distilled water or 0.05*N* HCl were used.

Spectrophotometric analysis of kynurenine showed the presence of two major maxima at wave lengths of 227 and 360 mμ and one minor peak at a wave length of 260 mμ. Calculations of elution data varied according to the O. D. readings of either one of the major maxima. In general, calculations from the O. D. at 360 mμ were much higher than those at 230 mμ. Our data indicates that the shorter wave length is more accurate for quantitative determinations. The differences (230–220 mμ) varied with the pH of the eluant. It is reduced to a minimum at acidic pH's and is more pronounced in the alkaline range (Fig. 3). With acetate buffer, the O. D. of the buffer itself could obscure the difference.

TABLE I

KYNURENINE SPECTROPHOTOMETRIC CONSTANTS AT DIFFERENT pH VALUES

pH	*$O.D._{230}$-$O.D._{220}$*	*$O.D._{220}$-$O.D._{275}$*	*$O.D._{230}$-$O.D._{300}$*	*$O.D._{360}$-$O.D._{300}$*	*$O.D._{360}$-$O.D._{230}$*
1.00(HCl)	0.210	0.83	1.173	0.165	0.20
1.00(H_2SO_4)	0.204	0.77	0.852	0.117	0.177
2.2(HAc)	0.225	0.92	0.855	0.145	0.211
3.60	0.110	0.88	0.810	0.115	0.207
3.80	0.140	0.84	0.800	0.120	0.209
4.20	0.095	0.89	0.805	0.125	0.200
4.80	0.124	0.87	0.790	0.115	0.228
5.28	0.222	0.59	0.524	0.155	0.295
5.90	0.202	0.56	0.451	0.145	0.321
6.46	0.194	0.69	0.549	0.148	0.269
6.80	0.169	0.74	0.635	0.154	0.242
7.16	0.132	0.82	0.676	0.120	0.215
8.04	0.194	0.77	0.769	0.118	0.180
13.00	0.262	0.34	0.373	0.072	0.228

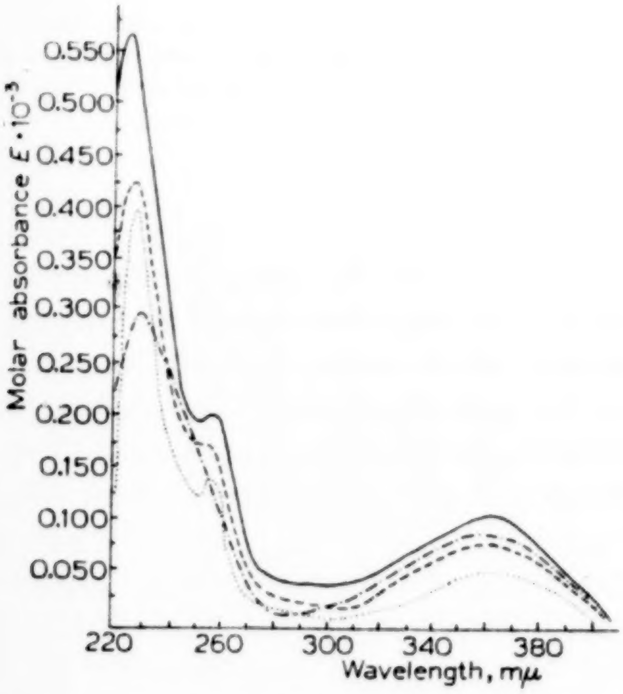


Fig. 3. Ultraviolet spectra of kynurenine. 1. In distilled water: ————————; 2. In 0.05*N* HCl: — — — — — — —; 3. In 0.05*N* NaOH: · · · · · · · · · ·; 4. In 0.05*N* H_2SO_4: (— · — · —·)

TABLE II

TRYPTOPHAN SPECTROPHOTOMETRIC CONSTANTS AT DIFFERENT pH

pH	*$O.D._{min}$-$O.D._{max}$*	*$O.D._{max}$-$O.D._{min}$*
1.00(HCl)	0.360	0.390
1.00(H_2SO_4)	0.370	0.391
2.20(HAc)	0.324	0.946
3.60	0.325	0.918
3.80	0.320	0.959
4.20	0.318	0.968
4.80	0.316	1.013
5.28	0.176	0.934
5.90	0.157	0.948
6.46	0.214	0.880
6.81	0.249	0.887
7.16	0.288	0.845
7.73	0.339	0.799
8.04	0.347	0.790
13.00	0.322	0.393

Variations in the constants of the spectral curve of kynurenine and tryptophan at different pH's are presented in Tables I and II. These variations indicate changes in the extinction coefficient of kynurenine and tryptophan exposed to these different pH conditions. These changes were brought about by the effect of salt concentration, hydrogen-ion concentration and conductivity of the electrolyte used.

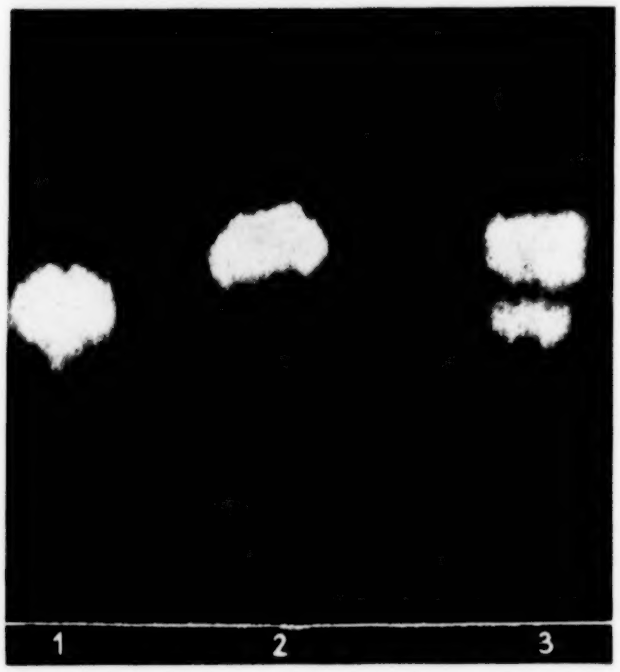


Fig. 4. Resolution of tryptophan isomers on paper chromatography. Whatman No. 1 filter paper was developed with methanol–water solvent (9 : 1) for 48 h, dried and examined as described in text. 1. *l*-tryptophan; 2. *d*-tryptophan; 3. *dl*-tryptophan.

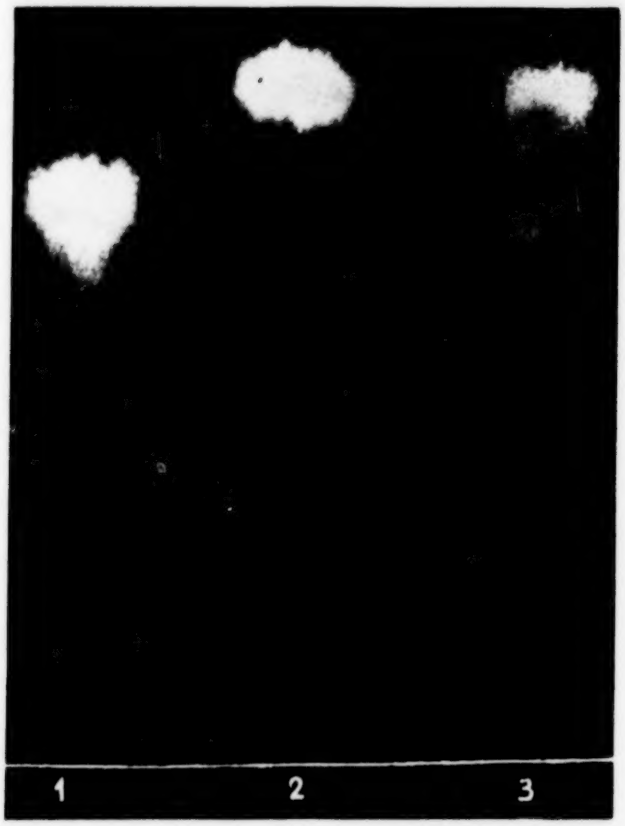


Fig. 5. Resolution of kynurenine isomers on paper chromatography. Whatman No. 1 filter paper was developed with methanol–water solvent (9 : 1) for 48 h, dried and examined as described in text. 1. *l*-kynurenine; 2. *d*-kynurenine; 3. *dl*-kynurenine.

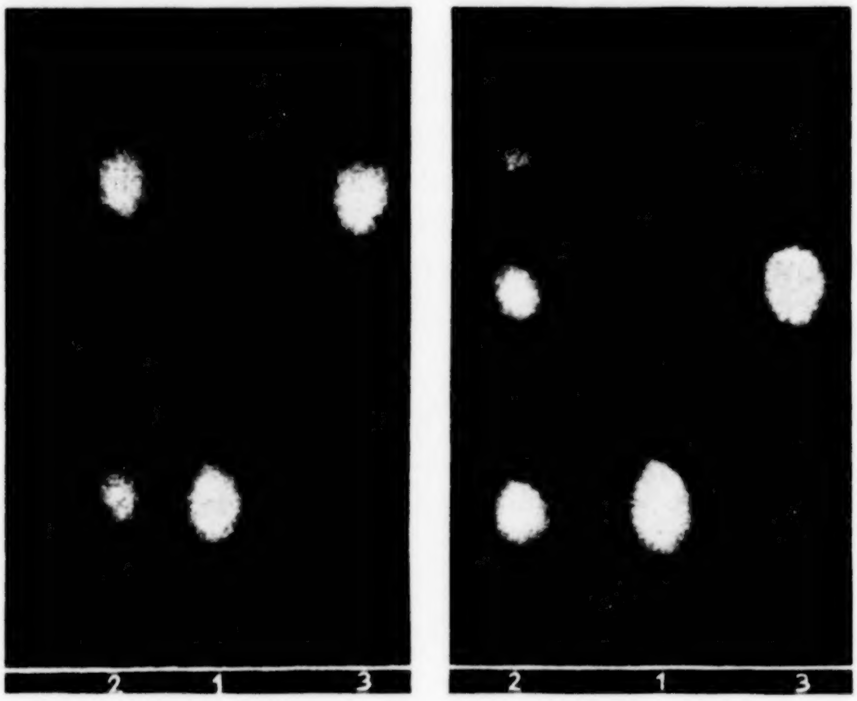
Ultraviolet irradiation of d-, l-, or dl-tryptophan

Aqueous solutions containing *d*-, *l*-, or *dl*-tryptophan ($0.5\,M$) when irradiated by ultraviolet light produce breakdown of tryptophan. *d*-kynurenine (from *d*-tryptophan), *l*-kynurenine (from *l*-tryptophan) and *dl*-kynurenine (from *dl*-tryptophan) were identified among the breakdown products. Ultraviolet light results in a decreased pH of the aqueous solutions, and in changes of spectral characteristic curve of tryptophan. The solutions acquire a color and on standing at 0° in the refrigerator, a faint odor is produced.

A Mineralight model V-41, with short wave ultraviolet (2537 Å) six bar quartz tube and special short-wave filter producing 45 mW per square foot was used as a source of the ultraviolet light.

Figs. 4 and 5 are chromatograms developed in methanol–water (9 : 1) solvent, demonstrating the resolution of *d*-, *l*-, and *dl*-tryptophan as well as the resolution of *d*-, *l*-, and *dl*-kynurenine respectively.

Figs. 6a and 6b are chromatograms developed in the methanol–water solvent, irradiated *d*-tryptophan, *d*-kynurenine being one of the products (Fig. 6a). *l*-tryptophan is converted into *l*-kynurenine by ultraviolet irradiation and is presented in Fig. 6b. The chemical identity of remaining products of irradiation was well as the effect of pH, ionic strength of the solutions on the rate of tryptophan breakdown, etc., will be reported in the near future.



a b

Fig. 6. (A) Action of ultraviolet light on *d*-tryptophan. A chromatogram developed in methanol–water solvent showing the conversion of *d*-tryptophan to *d*-kynurenine. 1. *d*-tryptophan; 2. *d*-tryptophan after ultraviolet irradiation (*i.e.*, *d*-kynurenine); 3. *d*-kynurenine (pure chemical). (B) Action of ultraviolet light on *l*-tryptophan. A chromatogram developed in methanol–water solvent showing the conversion of *l*-tryptophan to *l*-kynurenine. 1. *l*-tryptophan; 2. *l*-tryptophan after ultraviolet irradiation (*i.e.*, *l*-kynurenine); 3. *l*-kynurenine (pure chemical).

DISCUSSION

The resolution of *d*-, *l*-tryptophan and kynurenine on paper chromatography and paper electrophoresis is investigated. The resolution of the isomers of tryptophan and kynurenine is due to absorption of the amino acids on the surface of the optically activated cellulose of the filter paper. Such optical activation of cellulose could be induced by the specific chromatographic (organic) solvent used, *i.e.*, methanol.

Elution of tryptophan or kynurenine from chromatograms or electrograms varied with the pH of the eluant. The data obtained indicates that the best eluant for tryptophan and kynurenine from electrograms is either sterile distilled water of NaOH–$NaHCO_3$.

Using the ultraviolet spectrophotometric procedure described here in the determination of tryptophan and kynurenine, the data suggests that better determinations are obtained if the exact maximum wave length is used in calculation.

The nature of the chemical substances produced by the action of ultraviolet radiation on *d*-, *l*-, or *dl*-tryptophan, and on *d*-, *l*-, or *dl*-kynurenine indicates that tryptophan was degraded gradually into a series of products. The products identified from

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the degradation of tryptophan are *d*-kynurenine (from *d*-tryptophan) and *l*-kynurenine (from *l*-tryptophan). Another product was identified in both tryptophan and kynurenine irradiated aqueous solutions. The kinetics of the reaction as well as the chemical identity of the resulting products are being studied.

Over recent years evidence has accumulated to emphasize the important role of radiation on many enzyme systems. In particular the radiation influence on certain hereditary material has been noted.

Several investigators[4-6] have studied the action of x-rays on aqueous solutions of deoxyribonucleic acid and have observed physical effects such as a decrease in the viscosity of the solutions. SCHOLES *et al.*[7,8] reported on the chemical effects of x-radiation on aqueous solutions of deoxyribonucleic acids and ribonucleic acids. The effect of radiation was interpreted as action of free radicals initiated by the action of the radiation on solvent in the following process[9-11]:

$$H_2O \longrightarrow H^+ + OH^-$$

SUMMARY

The factors affecting the ultramicrodetermination of tryptophan and kynurenine were investigated by paper electrophoresis, paper chromatography and spectrophotometry. The electrolyte used in electrophoresis influences the mobility, the separation and the ultraviolet spectra of tryptophan and kynurenine. The pre-treatment of filter paper for chromatography did not influence the R_F of tryptophan and kynurenine, but interfered with their quantitative determination. The effect of ultraviolet irradiation of *d*-, *l*-, and *dl*-tryptophan as well as *d*-, *l*-, and *dl*-kynurenine was studied.

RÉSUMÉ

Les facteurs intervenant lors de l'ultramicrodosage du tryptophane et de la kynurenine ont été examinés par électrophorèse sur papier, chromatographie sur papier et par spectrophotométrie.

ZUSAMMENFASSUNG

Die Faktoren, welche die Ultramikro-Bestimmung von Tryptophan und Kynurenin beeinflussen, wurden mit Hilfe der Papierelektrophorese, Papierchromatographie und Spektrophotometrie untersucht.

REFERENCES

[1] R. L. BOWMAN, P. A. CAULFIELD AND S. UDENFRIEND, *Science*, 122 (1955) 32.
[2] A. A. HAKIM, *Arch. Biochem. Biophys.*, 70 (1957) 591.
[3] A. A. HAKIM, *Anal. Chim. Acta*, 17 (1957) 439.
[4] F. WEGMULLER, *Ph.D. Thesis*, Berne, 1946.
[5] A. H. SPARROW AND F. M. ROSENFELD, *Science*, 104 (1946) 245.
[6] B. TAYLOR, J. P. GREENSTEIN AND A. HOLLANDER, *Arch Biochem.*, 16 (1948) 19.
[7] G. SCHOLES, G. STEIN AND J. WEISS, *Nature*, 164 (1949) 709.
[8] G. SCHOLES AND J. WEISS, *Nature*, 166 (1950) 540.
[9] J. WEISS, *Nature*, 153 (1944) 748.
[10] J. WEISS, *Trans. Faraday Soc.*, 43 (1947) 314.
[11] J. WEISS, *Brit. J. Radiol., Suppl.*, 1 (1947) 56.

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SPECTROPHOTOMETRIC DETERMINATION OF LANTHANUM WITH NEO-THORONE

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INTRODUCTION

Although alizarin red S[1] is generally used as a colorimetric reagent for lanthanum, the colour reaction is not very sensitive, and other reagents such as hematoxylin[2] have also been applied.

In the present work, the thorium-complexing agent, 2-ortho-arsonophenyl-azo-2 (1,8-dihydroxynaphthalene-3,6-disulphonic acid)[3], neo-thorone[4-7], has been successfully utilized for direct spectrophotometric determination of microgram amounts of lanthanum. The method is based on the fact that lanthanum forms a reddish-violet water-soluble complex with neo-thorone which is stable in acidic or basic medium. The optimum conditions for the procedure are discussed below.

EXPERIMENTAL

Reagents

A solution of the pure sodium salt of 2-ortho-arsonophenyl-azo-2-(1,8-dioxynaphthalen-3,6-disulphonic acid) — neo-thorone — was prepared according to ISHIBASHI AND HIGASHI[4]. Neo-thorone (0.1 g) was dissolved in 100 ml of water.

A standard solution of lanthanum was prepared by dissolving 0.78 g of chemically pure lanthanum nitrate tetrahydrate (Merck's reagent) in distilled water and diluting to 250 ml. This solution containing 1.001 mg of lanthanum per ml was standardized gravimetrically as lanthanum oxide. It diluted to give solutions containing μg-amounts of lanthanum per ml. All other chemicals used in this work were pure Merck's reagents.

Apparatus and technique

A Hitachi EPV-II spectrophotometer with cells of 1-cm path length was used for all measurements. All solutions were diluted to a final volume of 25 ml before transference to the absorption cells. The pH was measured with a Beckman H-2 type pH meter and adjusted by adding sodium acetate–acetic acid or ammonium chlorid–ammonia buffer solution.

RESULTS AND DISCUSSION

Absorption curves

Measured against a water blank, the absorption of the organic reagent (A in Fig. 1) and of a similar solution containing lanthanum (B in Fig. 1) indicated a shift of the absorption band towards longer wavelengths on the addition of lanthanum. The reagent plus lanthanum was measured against the solution of the reagent, B—A (C in Fig. 1). The predicted curve was obtained showing a maximum absorption at 570–575 mμ. The data are plotted in Fig. 1.

Effect of various amounts of reagent

The absorption of a series of solutions of pH 9.0, each containing 52 μg of lanthanum per 25 ml with varying amounts of reagent, was measured to determine a suitable concentration of the reagent. The results (Fig. 2) indicate that 2.0 ml of an aqueous 0.1% solution suffice to complex 0.05 mg of lanthanum in 25 ml of solution.

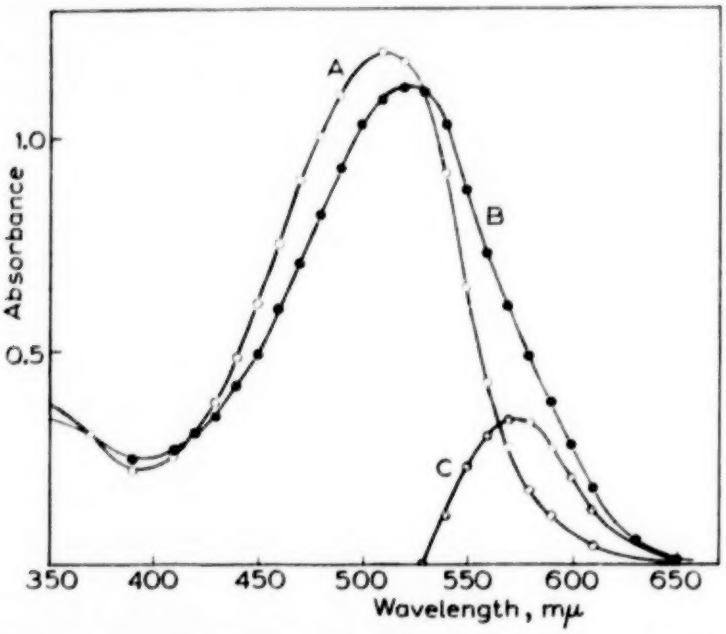

Fig. 1. Absorption spectra of neo-thorone; 25 ml final volume, Hitachi EPV-II spectrophotometer, slit width 0.05 mm. A: Reagent against water; B: Reagent plus lanthanum against water; C: Reagent plus lanthanum against reagent.

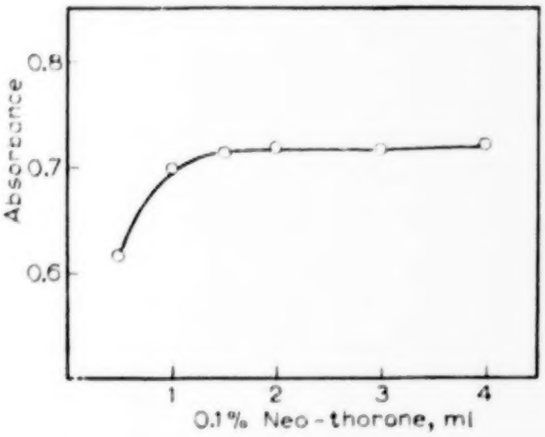

Fig. 2. Effect of neo-thorone concentration on absorbance; 52 μg La taken, correction applied for blank.

Effect of pH

Solutions containing lanthanum and reagent were adjusted to various pH values with sodium acetate–acetic acid or ammonium chloride–ammonia buffer solutions. Between pH 8.0 and 9.0 the absorption remained approximately constant; above 9.0, it decreased rapidly (Fig. 3).

Effect of time, light and temperature

The colour of the lanthanum–neo-thorone complex in aqueous medium was fully developed after a few min, and the absorbance was unchanged for at least 4 h (Table I). Thus the system is sufficiently stable for quantitative determinations. The absorbance of the complex solution remained almost constant for 4 h under normal conditions of light and temperature (20–30°).

Beer's law

The coloured solution obeys Beer's law giving a standard curve, a straight line (see Fig. 4) passing through the origin with an absorbance of 0.684 for 50 μg of lanthanum.

Sensitivity

The sensitivity of the colour reaction is either 0.008 μg lanthanum per cm² (practical) or 0.0029 μg lanthanum per cm² (according to SANDELL's definition).

TABLE I

VARIATION OF ABSORBANCE WITH TIME 2 ml OF 0.1% REAGENT IN WATER PLUS 15, 20, 25 μg OF LANTHANUM MEASURED *vs.* REAGENT AT pH 9.0, 570 mμ

time	*absorbance*		
min	*15 μg*	*20 μg*	*25 μg*
15	0.210	0.280	0.350
45	0.208	0.275	0.347
75	0.208	0.275	0.347
105	0.208	0.275	0.348
130	0.207	0.275	0.345
240	0.207	0.275	0.347

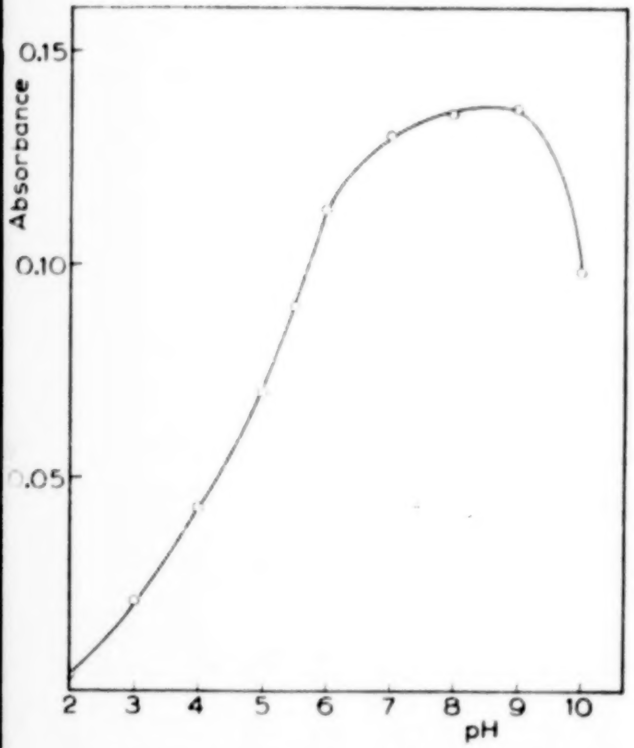

Fig. 3. Variation of absorbance with pH.

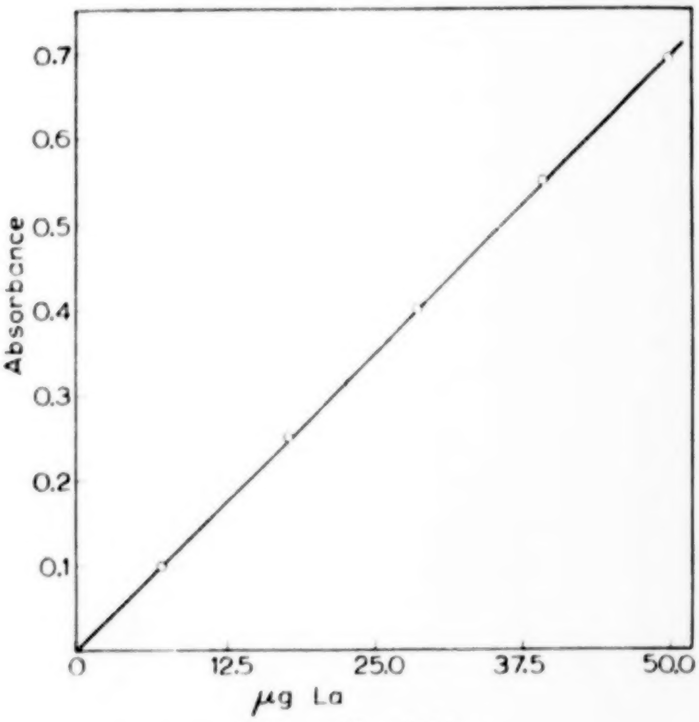

Fig. 4. Beer's law.

Experimental procedure

Aliquots of 0.5, 1.0, 1.5, . . . 5 ml of standard solution containing 10 μg of lanthanum per ml, were pipetted into 25-ml volumetric flasks. To each flask 5 ml of pH 9.0 buffer solution and 2 ml of 0.1% neo-thorone solution were added. The solutions were diluted to 25 ml with distilled water. A reference solution was prepared with reagent. The samples were then transferred to the absorption cells, and their absorbances were measured in a Hitachi EPV-II spectrophotometer.

Interferences

The effects of nearly all the elements associated with lanthanum were studied to determine their behaviour with neo-thorone under the optimum conditions used above.

Citric and tartaric acids, oxalate, phosphate, and perchlorate even in minute amounts, interfered with the colour development.

Up to 400 μg of fluoride and up to 50 mg of acetate, sulfate, chloride and nitrate, as their sodium, potassium, or ammonium salts, did not interfere.

Many cations, *e.g.* aluminium, copper, iron(III), thorium, cerium and uranium, interfered by forming complexes with neo-thorone.

Studies on the separation of lanthanum from the interfering substances will be published later.

Composition of the coloured complex of lanthanum-neo-thorone

The empirical formula of the coloured complex of lanthanum was determined by adopting the "continuous variation" and "mole ratio" methods. Absorbance measurements at the wavelength of maximum absorption for the lanthanum complex were made within 5 minutes of preparing the solutions. Within experimental error, the results (Figs. 5 and 6) suggest a 1 : 3 complex of lanthanum with the reagent.

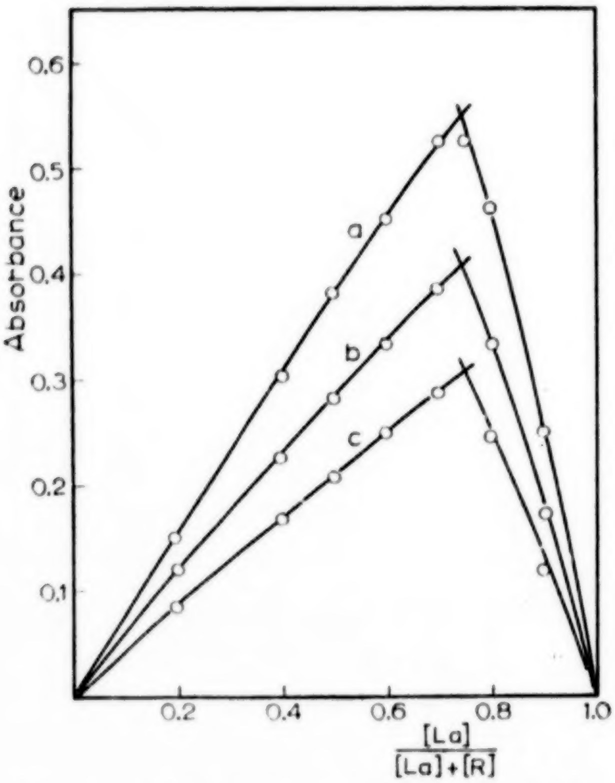

Fig. 5. Continuous variation method: reddish-violet complex of lanthanum and neo-thorone, pH 9.0, a. 570 mμ, b. 590 mμ, c. 600 mμ, [R] = [La] = $1.74 \cdot 10^{-4}$ *M*.

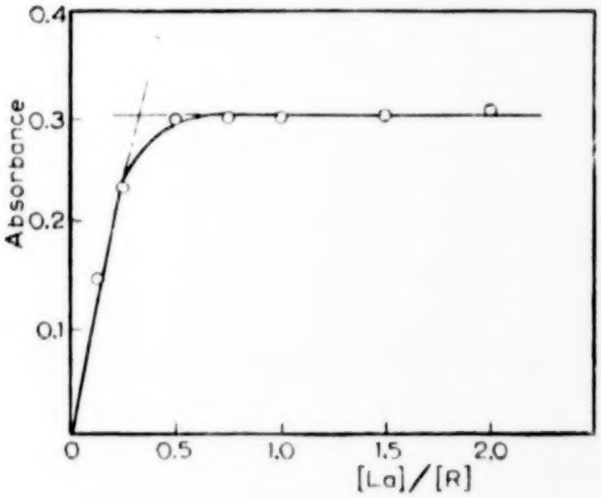

Fig. 6. Mole-ratio method; pH 9.0, 570 mμ, [R] = [La] $1.74 \cdot 10^{-4}$ *M*

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Prof. M. ISHIBASHI of the Kyoto university for his kind advice.

SUMMARY

A method has been developed for the spectrophotometric determination of microgram amounts of lanthanum by means of neothorone, 2-ortho-arsonophenyl-azo-2-(1.8-dioxynaphthalen-3,6-disulphonic acid). The method is sensitive, and as little as 2 μg of lanthanum can be determined in 25 ml of final volume. The calibration curve conforms to Beer's law. The stoichiometric composition of the coloured complex has been determined.

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RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage du lanthane au moyen du néothoron, acide arsonophényl-2-azo-2(dihydroxy-1,8-naphtalène disulfonique-3,6). Ce procédé est sensible et permet de doser jusqu'à 2 μg de lanthane dans 25 ml. La composition stoechiométrique du complexe a été déterminée.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode beschrieben zur Bestimmung von Lanthan mit Hilfe von ,,Neothoron'', 2-ortho-arsenophenyl-azo-2 (1.8-dioxynaphtalen-3.6-disulfosäure). Diese Reaktion erlaubt die Bestimmung von 2 μg Lanthan in 25 ml Lösung. Die stöchiometrische Zusammensetzung des gefärbten Komplexes wird angegeben.

REFERENCES

[1] I. M. KOLTHOFF AND R. ELMQUIST, *J. Am. Chem. Soc.*, 53 (1931) 1217.

[2] T. P. SARMA AND BH. S. V. RAGHAVARAO, *J. Sci. Ind. Research* (*India*), 14B (1955) 450.

[3] V. I. KUZENETSOV, *Compt. rend. acad. sci. U.R.S.S.*, 31 (1941) 898.

[4] M. ISHIBASHI AND S. HIGASHI, *Japan Analyst*, 4 (1955) 14; 5 (1956) 135.

[5] K. EMI AND J. HAYAMI, *J. Chem. Soc. Japan Pure Chem. Sect.*, 76 (1955) 1291.

[6] S. SHIBATA AND T. MATSUMAE, *Bull. Chem. Soc. Japan*, 31 (1958) 377; 32 (1959) 279.

[7] S. SHIBATA, F. TAKEUCHI AND T. MATSUMAE, *Bull. Chem. Soc. Japan*, 31 (1958) 888.

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SUR LE DOSAGE DU CHROME DANS LES PRODUITS DE L'INDUSTRIE DU CIMENT

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INTRODUCTION

Dans un mémoire publié en 1950, JAEGER ET PELLONI[1] ont indiqué que les personnes atteintes d'eczéma au ciment réagissent positivement au test épicutané au bichromate de potassium. Cette observation a amené ces auteurs à admettre que l'eczéma au ciment n'est pas causé par la basicité du ciment, comme on l'avait supposé auparavant, mais qu'il est dû à la présence de chromates dans les ciments.

A la suite de ces constatations, nous avons examiné un certain nombre de ciments en vue de déceler des traces de chromates. La plupart des produits analysés ont donné en effet des réactions positives. Une orientation sur l'ordre de grandeur de la teneur en chromate nous a montré que les ciments contiennent en général quelques millionièmes de Cr(VI), donc quelques mg Cr(VI) par kg de ciment sous forme d'anion CrO_4^{-2} soluble dans l'eau.

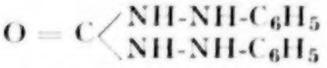
Il était important d'établir l'origine de l'élément chrome contenu dans les ciments. Certains auteurs ont admis que les traces de chrome proviennent de l'usure des appareils en acier chromé utilisés dans la fabrication du ciment (concasseurs, broyeurs, etc.). D'autre part, il fallait envisager la présence de chrome dans les matières premières servant à la fabrication du ciment.

Pour trancher la question, il était nécessaire d'élaborer des méthodes d'analyse permettant de doser de très faibles quantités de chrome dans les diverses matières utilisées pour la fabrication du ciment. Ces méthodes concernent:

A. le dosage du chrome total,
B. le dosage du chrome hexavalent (anion CrO_4^{-2}).

A. DOSAGE DU CHROME TOTAL

Pour l'identification de l'anion chromate, on utilise couramment la diphénylcarbazide



$$O = C\begin{matrix} \diagup NH\text{-}NH\text{-}C_6H_5 \\ \diagdown NH\text{-}NH\text{-}C_6H_5 \end{matrix}$$

qui donne avec le CrO_4^{-2}, en milieu acide, une coloration violette intense[2]. Cette réaction est très sensible; elle se prête non seulement à l'identification du chromate, mais aussi au microdosage du chrome[3,4].

Nous avons appliqué cette réaction pour doser des traces de chrome dans l'oxyde de titane[5] et pour déterminer la teneur en chrome des rubis[6].

Le dosage du chrome total dans les produits employés et fabriqués par l'industrie du ciment comprend les opérations suivantes:

I. Désagrégation de la matière à analyser
II. Oxydation du Cr(III) en Cr(VI)
III. Dosage colorimétrique de l'anion CrO_4^{-2}.

Nous avons examiné plusieurs procédés de désagrégation en vue de trouver une méthode appropriée pour solubiliser les ciments et les matières premières utilisées pour leur fabrication[7,8]. Dans une étude se rapportant à la préparation et l'analyse du corindon[6], nous avons reconnu les grands avantages que présentent des désagrégations par fusion avec du borax. Cette méthode convient également pour solubiliser les produits de l'industrie du ciment. Le mode opératoire est indiqué ci-dessous.

Les essais qui visaient l'oxydation du Cr(III) en Cr(VI) par une fusion oxydante n'ont pas donné de résultats satisfaisants. Nous avons constaté qu'il est préférable d'oxyder le Cr(III), après solubilisation, par l'addition de persulfate de potassium et de nitrate d'argent, ce dernier sel agissant comme catalyseur.

L'anion CrO_4^{-2} obtenu de cette manière est dosé colorimétriquement après addition de diphénylcarbazide en milieu sulfurique. Cette dernière opération est délicate, car la coloration violette que donne le réactif n'est pas stable. Nous disposions d'un colorimètre Klett-Summerson qui convient parfaitement à ce genre de dosages.

A la suite de nombreux essais que nous avons exécuté, nous avons adopté le mode opératoire suivant pour le dosage du chrome total dans le ciment.

I. Désagrégation

Une prise d'env. 0,5 g de matière à analyser (ciment ou autre matière finement pulvérisée) est introduite dans un creuset de platine. On calcine à 800–900° au Teclu ou au four électrique pendant 20 à 30 min pour détruire les matières organiques qui peuvent se trouver dans le produit.

Après refroidissement, on ajoute 5 g de borax anhyde $Na_2B_4O_7$. (Le produit commercial „borax fondu" est pilé préalablement dans un mortier de porcelaine.) Le ciment et le fondant sont intimement mélangés. On chauffe sur Teclu jusqu'à fusion complète du borax, puis on agite légèrement le creuset pour homogénéiser son contenu.

On calcine fortement pendant env. 1 h (pleine flamme du Teclu ou four électrique, température env. 900°).

On retire le creuset du four et, par un mouvement giratoire, on provoque la solidification de la masse en couche mince sur la paroi du creuset. (Il faut éviter la formation d'un bloc compact qui détériorerait le creuset.)

Après refroidissement, on introduit le creuset dans un bécher contenant env. 250 ml de H_2SO_4 2 *N*. On chauffe au bain-marie pendant env. 8 h (ou une nuit). Le produit de désagrégation étant dissous, on retire le creuset et on le rince avec quelques ml d'eau distillée.

II. Oxydation

On ajoute à la solution sulfurique de la désagrégation 3 ml de $AgNO_3$ 0.1 *N* et 0.5 g de $K_2S_2O_8$ et on abandonne au bain-marie pendant 20–30 min.

On laisse refroidir, puis on neutralise par NH_3 conc. jusqu'à pH 7-9.

Remarque: Une coloration violette provient de l'oxydation du Mn^{+2} en MnO_4^-. Elle disparaît pendant l'opération qui suit.

Il y a précipitation de $Fe(OH)_3 + Al(OH)_3$. On chauffe au bain-marie pour coaguler le précipité et on évapore jusqu'à un volume d'env. 150 ml. Après refroidissement, on filtre en recueillant le filtrat directement dans un ballon jaugé de 250 ml. On lave avec de l'eau distillée et on neutralise par H_2SO_4 2 *N*; finalement on acidifie la solution par 25 ml de H_2SO_4 2 *N* et on complète au trait de jauge avec de l'eau distillée. (Pour le dosage colorimétrique, il faut que l'acidité de la solution soit 0.2 *N*.)

III. Dosage colorimétrique de l'anion CrO_4^{-2}

On utilise pour l'étalonnage des solutions standard de $K_2Cr_2O_7$.

Solution standard A: 0.566 g $K_2Cr_2O_7$ par l (1 ml contient 200 μg Cr).

Solution standard B: 0.0283 g $K_2Cr_2O_7$ par l (1 ml contient 10 μg Cr).

La solution B n'est pas stable; elle se prépare au moment de l'emploi par dilution de la solution A dans la proportion 1 : 20.

Pour le dosage du CrO_4^{-2} dans la solution obtenue sous II, on prélève d'abord une prise de solution (par exemple 10 ml) pour établir au colorimètre la „valeur à blanc" de la solution.

On ajoute au restant de la solution contenue dans le ballon jaugé 4 ml de diphénylcarbazide.

Préparation du réactif: On dissout 0.25 g de diphénylcarbazide dans 50 ml d'acétone, puis one complète à 100 ml par de l'eau. Cette solution ne se conserve pas, il faut donc toujours utiliser une solution fraîche préparée le jour de l'emploi.

La coloration violette provenant de l'action de la diphénylcarbazide sur l'anion CrO_4^{-2} se développe lentement. Elle atteint son maximum après env. 10 min.

L'analyse colorimétrique, qui doit se fair 10–15 min après l'addition du réactif, donne la quantité de Cr(VI) par ml de solution.

On obtient la teneur en chrome de la prise soumise à l'analyse en multipliant le résultat par 254 (volume de la solution 250 ml + réactif 4 ml).

Remarques:

1. Pour obtenir des résultats corrects, il est nécessaire de faire le dosage colori-

métrique le plus rapidement possible après l'acidification du filtrat ammoniacal (maximum admissible 30 min).

2. Pour toutes les opérations, on doit utiliser de l'eau distillée exempte de matières réductrices. (Distiller l'eau en présence d'un peu de $KMnO_4$.) L'acide sulfurique est débarassé de matières réductrices par chauffage jusqu'à dégagement de vapeurs blanches épaisses.

3. La méthode indiquée ci-dessus permet de doser le chrome avec une précision relative de quelques %. Il arrive que certains dosages donnent des résultats inexacts, sans qu'on puisse en indiquer les causes. C'est pourquoi nous faisons toujours au moins 3 dosages pour chaque produit. Si un des résultats s'écarte de plus de 5% de la moyenne, ils est recommandé de refaire l'analyse avec de nouvelles prises.

B. DOSAGE DU CHROMATE SOLUBLE DANS LE CIMENT ET LE CLINKER

Nous nous sommes rendu compte que les matières premières utilisées pour la fabrication du ciment ne renferment pas de chrome hexavalent; par contre, on y trouve des quantités appréciables de chrome trivalent.

L'anion chromate se forme pendant la cuisson. Il a été constaté que les ciments fabriqués au four rotatif contiennent en général nettement plus de chromate que les ciments des fours à cuve.

Les ciments peuvent contenir, à côté de constituants oxydants (tel que l'anion CrO_4^{-2}), certaines matières réductrices. Si ces dernières sont solubles dans l'eau, elles peuvent provoquer des perturbations lors du dosage du chrome hexavalent dans l'extrait aqueux. Les diverses variantes que nous indiquons ci-dessous pour le dosage de l'anion chromate dans les ciments et les clinkers peuvent, par conséquent, donner des résultats différents.

Nous considérons le résultat le plus élevé que donne l'une des méthodes comme valeur la plus probable de la teneur en chromate.

Méthode I

Une prise de 15 à 20 g de ciment est introduite dans un ballon Stohmann contenant env. 250 ml d'eau distillée exempte de matières réductrices. On agite pour obtenir une suspension homogène, on complète avec de l'eau jusqu'au trait de jauge (500 ml) et on fait tourner le ballon Stohmann dans l'agitateur selon WAGNER pendant env. 20 min (20 tours par min).

Après décantation, on dose l'anion chromate dans une prise aliquote de la solution limpide.

Exemple: Prélever 25 ml dans un ballon jaugé de 100 ml, neutraliser avec H_2SO_4 2 *N*, puis acidifier avec 10 ml H_2SO_4 2 *N*; ajouter 2 ml de diphénylcarbazide et compléter à 100 ml avec de l'eau. Dosage colorimétrique après 10 min.

Méthode II (variante de la méthode I)

On extrait le chromate comme sous I, mais au lieu de laisser décanter, on filtre immédiatement sur filtre plissé.

A une prise aliquote du filtrat (par exemple 25 ml), on ajoute d'abord 2 ml de diphénylcarbazide, ensuite, par petites portions, H_2SO_4 *N* jusqu'à réaction acide. On dilue à 100 ml et on dose le chromate colorimétriquement.

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Méthode III

Dans un bécher de 100 ml contenant une prise de 50 g de ciment on ajoute, à l'aide d'une pipette, 30 ml d'eau. On agite avec une baguette de verre jusqu'à ce qu'on obtienne une pâte homogène, puis on laisse reposer 10 min. On fait couler la pâte sur un entonnoir en porcelaine et on filtre sous vide (filtre quantitatif, bande bleue) sans laver le précipité.

Dans une prise du filtrat, on dose le CrO_4^{-2} colorimétriquement après addition de H_2SO_4 et de diphénylcarbazide.

Remarque: La méthode III donne souvent des résultats légèrement plus faibles que la méthode I.

Méthode IV (variante de la méthode III)

On garnit un entonnoir de porcelaine (ø env. 4-6 cm) avec un papier filtre (bande bleue) humecté avec un peu d'eau. On introduit une prise de ciment de 20 à 30 g qu'on répartit en une couche d'égale épaisseur. On verse soigneusement 25 ml d'eau distillée sur le ciment, puis on fait actionner la trompe à vide. Pendant cette opération, on laisse tomber de l'eau goutte à goutte sur le ciment.

TABLEAU I

EXEMPLES DE DOSAGES DE CHROME

	Chrome total mg Cr/kg	*Chrome hexavalent mg Cr(VI)/kg*	
		méthode I	*méthode III*
Ciment I provenant d'un four rotatif (ciment de composition courante)	54 54 56 56 moy. 56 56 56 58	7·2 7·4 moy. 7·4 7·5 7·5	5·9 6.0 moy. 6.0 6.0
Ciment II provenant d'un four rotatif (ciment particulièrement riche en chromate)	87 87 91 moy. 90 92 93	22.2 22.2 moy. 22.2 22.2	16.8 16.9 moy. 17.0 17·2
Ciment III provenant d'un four à cuve	53 54 moy 54 56	1.8 2.0 moy. 2.0 2.1	1.6 1.7 moy. 1.7
Calcaire	13 13 moy. 14 14 15		
Marne I (composition courante)	101 101 moy. 102 102 104		
Marne II (particulièrement riche en Cr)	253 253 moy. 258 260 265		

Avec 100 ml d'eau, on arrive ainsi à extraire pratiquement tout le chromate contenu dans le ciment. Dans cet extrait, on dose l'anion CrO_4^{-2} en ajoutant, à une prise aliquote, d'abord la diphénylcarbazide et ensuite H_2SO_4 2 *N* (comme méthode II).

Remarque. Le méthode IV convient particulièrement à la recherche et au dosage du chromate dans les ciments provenant de fours à cuve. Nous avons constaté que ces ciments renferment des réducteurs, par exemple l'anion sulfure, qui réduisent le Cr(VI) en Cr(III). La méthode IV offre les meilleures chances d'éviter ces perturbations. Il nous est arrivé que certains ciments donnaient des résultats négatifs pour la teneur en CrO_4^{-2} selon les méthodes I, II et III, mais indiquaient bien la présence de CrO_4^{-2} lorsqu'on opérait selon la méthode IV.

REMERCIEMENTS

Nous remercions le Fonds National Suisse de la Recherche Scientifique du subside qu'il nous a accordé pour l'étude de la teneur en chrome dans les ciments. D'autre part, nous exprimons nos remerciements à MM. G. DUPASQUIER, J. ENEZIAN, J. P. QUINCHE et E. VESCOVI qui ont collaboré à la mise au point des méthodes de dosage et qui ont exécuté un grand nombre d'analyses.

RÉSUMÉ

Pour le dosage de très faibles quantités de chrome dans les ciments et dans les matières premières servant à leur fabrication, les auteurs proposent une méthode qui comprend les opérations suivantes: Désagrégation par fusion avec du borax anhydre, dissolution de la masse de désagrégation dans H_2SO_4 dilué et oxydation du Cr(III) en Cr(VI) par $K_2S_2O_8$ + $AgNO_3$, précipitation du fer et de l'aluminium par addition de NH_3, dosage colorimétrique de l'anion CrO_4^{-2} en milieu sulfurique au moyen de la diphénylcarbazide.

Les ciments et les clinkers contiennent du chrome hexavalent sous forme d'anion CrO_4^{-2} soluble dans l'eau. Le dosage de CrO_4^{-2} se fait par colorimétrie dans l'extrait aqueux. Quatre méthodes d'extraction sont indiquées. La présence de matières réductrices dans les ciments peut provoquer des perturbations.

SUMMARY

A method is described for the determination of small amounts of chromium in cement. The cement is decomposed by fusion with borax and the chromium is converted into chromate. Upon addition of diphenyl-carbazide, a coloured complex is obtained, which can be determined colorimetrically.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung kleiner Mengen Chrom in Zement durch Aufschluss mit Borax und Überführung des Chrom-(3) in Chromat. Dieses gibt mit Diphenylcarbazid eine gefärbte Komplexverbindung, die kolorimetrisch bestimmt wird.

BIBLIOGRAPHIE

[1] H. JAEGER ET E. PELLONI, *Dermatologica*, 100 (1950) 207.

[2] F. FEIGL, *Spot Tests*, Tome I, 4ème éd., Elsevier Publishing Co., Amsterdam, 1954, p. 159.

[3] F. D. SNELL ET C. T. SNELL, *Colorimetric methods of Analysis*, Tome II, van Nostrand Co., New York, 1949, p. 274.

[4] E. B. SANDELL, *Colorimetric Determinations of Traces of Metals*, Interscience Publ. Inc., New York, 1944, p. 191.

[5] R. FLATT ET X. VOGT, *Bull. soc. chim. France*, [5] 2 (1935) 1985.

[6] R COSANDEY, *Thèse*, Lausanne, 1956.

[7] J. ENEZIAN, *Travail de diplôme*, Lausanne, 1953.

[8] E. VESCOVI, *Travail de diplôme*, Lausanne, 1954.

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ELECTRON TRANSFER SPECTRA IN COPPER AMMINES

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When the measurement of the absorption spectra of inorganic salts is extended far into the ultraviolet, an intense absorption-band is noticed in the region of 200 mμ[1]. In the case of transition metal ions the UV-band is several thousand times more intense than the visible band. These spectra are associated with the transfer of an electron between the ion and a water molecule in the hydration sphere, and have been named electron transfer spectra. For such a process to occur with reasonable probability, the two atoms must be bound together by comparatively strong forces, but the bonding must not interfere with the assignment of electrons to individual atoms, *i.e.*, the bonds must be of ionic or ion-dipole character rather than true atomic (electron-pair) bonds. The stronger the bond, the more energy is necessary to bring about an electron-transfer, and hence the absorption band appears at a shorter wavelength with stronger bonds.

The stable alkali and alkaline earth metal ions do not show any electron transfer band below the limit of observation in the usual spectrophotometer. The hydrated ions of other metals have been thoroughly studied by FROMHERZ *et al.*[2-4] and show fairly strong electron transfer bands. There is a large class of complex compounds in which the water molecules of the hydrates are replaced by other neutral molecules, particularly ammonia and ammines. It was expected that the ammines would show electron transfer bands of considerable intensity in the UV-region, but as ammines are stabler than the hydrates, these bands would probably be located at shorter wavelengths than in the hydrates. This is probably the reason why no systematic study of the electron transfer spectra of metal ammines has been reported.

It is known that in the case of metal ammines all the ammonia molecules are not bound to the metal ion equally strongly[5]. Particularly, in the case of copper hexammine two of the ammonia molecules are weakly bound and it is even doubtful if hexammine can exist in solution at all. It was surmised that the electron transfer bands would be located at longer wavelengths than the corresponding hydrates. To study this problem, the absorption spectra of a number of copper ammines were measured in the range of 200–250 mμ.

EXPERIMENTAL

E. Merck's G.R. quality reagents were used in all these measurements. The solvents were scrupulously purified to make them transparent in the region 200–250 mμ. The absorption spectra measurements were made in Hilger UV-speck and Beckman Spectrophotometer Model DU, using 1-cm matched silica cells.

DISCUSSION

An equilibrium between tetra, penta and hexammines may exist in the solution, hence its composition was uncertain and the extinction values had to be expressed in terms of the copper concentration rather than that of the complex. It was found that on that basis the extinction of the UV-bands shown in Fig. 1 was 6,000 to 14,000 times more intense than the visible band of copper at 790 mμ.

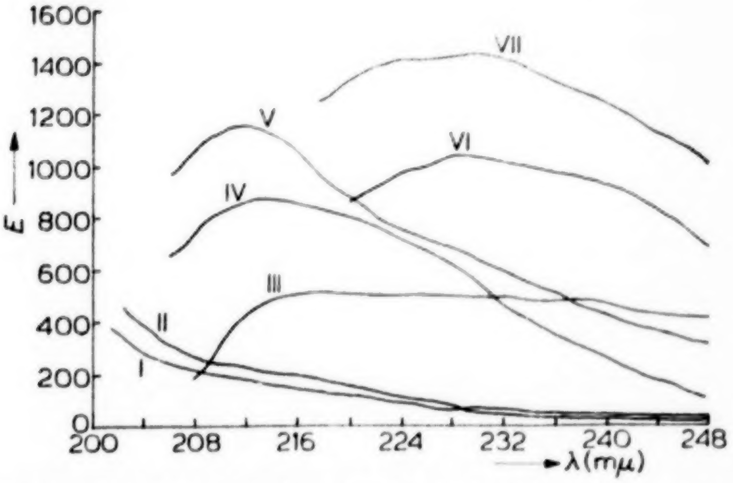

Fig. 1. Absorption spectra of copper ammines in the UV-region. Curve I: copper acetate (copper conc. 10^{-3} *M*); curve II: copper perchlorate (copper conc. 10^{-3} *M*); curve III: copper perchlorate–0.5 *M* methyl ammine (copper conc. 10^{-4} *M*); curve IV: copper perchlorate–0.5 *M* ammonia –0.5 *M* ammonium sulphate (copper conc. 10^{-4} *M*); curve V: copper perchlorate–0.5 *M* ammonia (copper conc. 10^{-4} *M*); curve VI: copper perchlorate–0.5 *M* ethylene diammine (copper conc. 10^{-4} *M*); curve VII: copper glycinate (copper conc. 10^{-4} *M*).

In order to suppress anion association copper was used as its perchlorate. In the case of ammines the ammonia concentration was at least 100 times that of copper to ensure the presence of copper in its highest coordination state. It can be seen from curves II and V that the ammine showed an absorption band at about 214 mμ, while the band for hydrate was located somewhere below 200 mμ. When ammonium sulphate was added to the solution of copper ammine, the band became diffuse and extinction was suppressed, but the peak appeared at about the same position. In the case of methylammine the band was broad an diffuse, extending from 212–240 mμ. With ethylenediammine the peak of the band shifted to 228 mμ, but the extinction was of the same order of magnitude as the simple ammine. The shape of the band suggests that actually two bands with peaks at 228 mμ and 234 mμ respectively were superimposed. Probably the two bands are associated with the cis- and trans-modifications of copper ethylene diammine dihydrate. In the case of ammines a similar difference between the cis- and trans-forms would be expected, but their sharpness is probably lost because of the superposition of penta- and hexammine bands.

In the case of copper glycinate the characteristic absorption band was found to be a superposition of two bands with peaks at 222 mμ and 230 mμ. In this case the electron transfer may take place between the copper and the amino or carboxyl groups of the glycine molecule. The absorption spectra of copper acetate in this region showed no peak and the extinction over the whole region was extremely low, indicating the absence of electron transfer between copper and carboxyl groups. It may be concluded that in glycinate the electron transfer takes place between copper and the amino groups.

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Most of the ammines can exist as hydrates in solution and the water molecules in these hydrates are much less tightly bound than in simple hydrates. The electron transfer observed may be between the metal ion and the water molecule in the co-ordination sphere rather than between the metal and the ammine group. It has been shown by DAINTON AND JAMES[6] that in the case of hydrates the electron transfer usually takes place from the metal to the water molecule. The H_2O^- formed decomposes to give H atoms, whose existence may be proved by the initiation of polymerisation of acrylonitrile. When an aqueous solution of acrylonitrile containing the copper ammine was irradiated with light of a wavelength corresponding to the peak of the characteristic absorption band, no polymerisation took place. This probably means that the electron transfer bands are not due to transition between metal and water but to transfer between metal and ammine group. However, the polymerisation of acrylonitrile may be inhibited by the ammines, so that the bands may actually be due to the former transition. It is difficult to reach a definite conclusion at this stage.

It has been demonstrated that in aqueous ammoniacal solution copper may exist as a hydroxo complex, $[Cu(NH_3)_3(OH)(H_2O)_2]^+$, especially if the solution be weak in ammonia. The situation in this complex is similar to anion association and there may be a strong electron transfer band owing to transition between copper and hydroxyl ions. Possibly, the intense UV-bands reported above are due to similar hydroxo complexes of copper. The copper ammine in a solution containing less than 0.1 *M* ammonia showed an absorption band at 275 mμ which was about 200 times more intense than the visible band but only a fifth of that at 214 mμ. In 0.5 *M* ammonia solution the band at 275 mμ was absent. It can be concluded that the 275 mμ band is due to hydroxo compound, while the bands in the vicinity of 212–230 mμ are in fact genuine ammine bands.

ACKNOWLEDGEMENT

Our sincere thanks are due to Dr. P. SENGUPTA, E.I.P.W. Ltd., Calcutta for his kind assistance during the course of this investigation with the absorption spectra measurements.

SUMMARY

The absorption spectra of ammine, ethylenediammine and methylammine complexes of copper as well as of copper glycinate in aqueous solution showed intense absorption bands in the region of 200–250 mμ. These bands have been associated with the electron transfer spectra between the copper and the ammine group. No unequivocal assignment of the direction of electron transfer could be made.

RÉSUMÉ

Les auteurs ont effectué une étude des spectres d'absorption des composés: cuivre-ammines, cuivre-éthylènediamine, cuivre-méthylamine et glycinate de cuivre.

ZUSAMMENFASSUNG

Es wurden die Absorptionsspektren von Kupferamminen, Kupfer-äthylendiamminen, Kupfer-methylamminen und Kupferglycinat in wässriger Lösung gemessen.

REFERENCES

[1] E. RABINOWITCH, *Revs. Modern Phys.*, 14 (1942) 112.
[2] H. FROMHERZ AND K. H. LIH, *Z. physik. Chem.*, A153 (1931) 321.
[3] H. FROMHERZ AND H. WALLS, *Z. physik. Chem.*, A178 (1936) 29.
[4] E. DOCHLEMAN AND H. FROMHERZ, *Z. physik. Chem.*, A171 (1934) 353.
[5] J. BJERRUM, *Metalammine Formation in Aqueous Solution*, Copenhagen, 1941.
[6] F. S. DAINTON AND D. G. L. JAMES, *J. chim. phys.*, 48 (1951) C17.

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THE DETERMINATION OF CYSTINE WITH *p*-AMINODIMETHYLANILINE

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The formation of a blue colour in the reaction between cysteine and *p*-aminodimethylaniline in the presence of ferric ions was observed first by FLEMING[1] and later developed into a quantitative procedure for the determination of cystine by VASSEL[2]. This method involves the reduction, in acid solution, of cystine to cysteine by zinc in the presence of the reagent and a ferric salt (which is also reduced); the colour is developed by adding an excess of ferric ions and heating. By reducing the cystine before the addition of the reagent and by using a larger quantity of zinc, MECHAM[3] increased the sensitivity and improved the reproducibility of this determination.

The main disadvantage of these methods is that the reagent blanks are strongly coloured and absorb appreciably at the wavelength of maximum absorption of the blue compound.

In the present investigation it has been found that the blue compound is extracted completely on shaking with iso-amyl alcohol. The extract is contaminated with a small amount of a brown impurity, probably oxidised *p*-aminodimethylaniline, but this may be extracted from the alcohol solution by aqueous alkali. The blue compound, which is believed to be a carboxy-benzothiazine[2], assumes a more intense colour on being rendered alkaline. Strong bases, like sodium or potassium hydroxide, cause the colour to become more red and less intense than does ammonium hydroxide; another advantage in using the weaker base is that it has less tendency to emulsify the alcohol during extraction. The addition of ammonium chloride also assists in preventing the formation of an emulsion.

The optimum conditions for the formation of the blue compound have been re-investigated using this extraction technique. The test is not very sensitive to changes in the concentrations of zinc, ferric and ferrous ions and *p*-aminodimethylaniline over a wide range but is very dependent on acid concentration. The maximum development of the blue colour occurs at a much lower concentration of acid than that recommended by VASSEL and MECHAM who may have used an excess of acid to suppress the colour due to ferric salts.

The colour, measured at maximum absorption, is more stable than that produced by previous methods; during a period of 5 days at room temperature, a constant rate of fading of about 1% per day was observed; the colour produced by VASSEL's method increased by 40% during the same period under the same conditions. The intensity of the colour in amyl alcohol decreases slightly with increase in temperature (about 4% per 10°) and for accurate work, measurements should be made at the temperature used for the calibration tests.

Mecham's reagent, which is prepared by reducing ferric ammonium sulphate with zinc in the presence of *p*-aminodimethylaniline, does not appear to have any advantage over the proposed reagent which is prepared directly from the ferrous salt and is stable for at least four weeks when stored in a brown glass bottle at room temperature.

Fig. 1 compares the absorption spectra of the coloured solutions obtained by Vassel's method (curve A), Mecham's method (B) and the present method (D). Curve C shows the present method without the alkali treatment of the alcohol extract. In each case the same weight of cystine was used and the final volumes were the same; measurements were made against the respective reagent blanks. The absorption spectra of these reagent blanks measured against the respective pure solvents (Fig. 2) illustrate the almost complete elimination of extraneous colour in the present method.

The results of twelve determinations performed on the same wool hydrolysate showed a maximum deviation from the mean of 0.4%. A series of tests in which known amounts of cystine were added to a cystine-containing protein hydrolysate gave results to within 1% of the calculated values. The proteins used for these tests were hydrolysed by refluxing with 6 *N* hydrochloric acid. Vassel claimed that formic acid in the hydrolysing mixture increased the colour intensity but, under the present conditions, the increase obtained by replacing half of the hydrochloric acid by an equivalent amount of formic acid was very small.

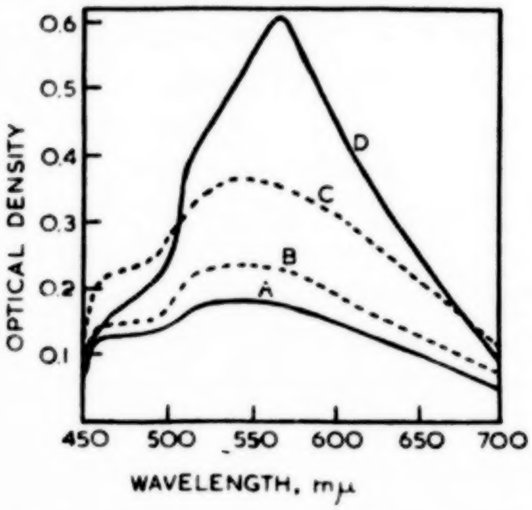

Fig. 1. Absorption spectra of test solutions measured against reagent blanks.

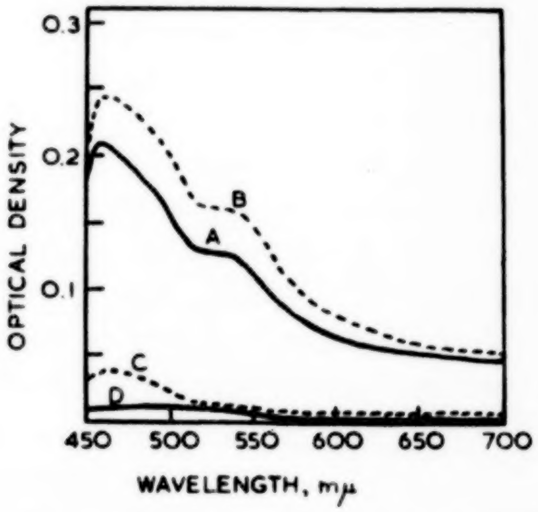

Fig. 2. Absorption spectra of reagent blanks measured against pure solvents.

A calibration curve may be prepared by using a solution of purified cystine in dilute hydrochloric acid.

Beer's Law remains valid up to 40 μg of cystine.

METHOD

Reagents

p-Aminodimethylaniline reagent. 24.0 g of $ZnSO_4 \cdot 7\ H_2O$ and 8.0 g of $FeSO_4(NH_4)_2SO_4 \cdot 6\ H_2O$ are dissolved in *N* H_2SO_4 and 0.04 g of *p*-aminodimethylaniline sulphate is added. The volume is made up to 100 ml with *N* H_2SO_4.

Ferric ammonium sulphate. 20.0 g of $Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24\ H_2O$ is dissolved in *N* H_2SO_4 to give 100 ml of solution.

Ammonia/ammonium chloride reagent. 10.7 g of NH_4Cl and 11.2 ml of 0.880 ammonia solution are made up to 100 ml with water.

REDUCTION OF CYSTINE

5 ml of a protein hydrolysate, containing between 0.2 and 0.4 mg of cystine and approximately 1.1 *N* with respect to hydrochloric acid, is added to 5 ml of concentrated hydrochloric acid in a boiling tube. 0.3 g of zinc dust is added and a Kjeldahl stopper is placed in the tube immediately. The tube is shaken occasionally until all the zinc is dissolved; this usually requires about 30 min. The tilted tube is rotated to wash down the sides. Cysteine should be determined soon after the reduction is completed.

DETERMINATION OF CYSTEINE

1 ml of the reduced cystine solution is measured into a boiling tube; an accurately calibrated glass 'walking-stick' pipette (Gallenkamp) is convenient for this purpose as this type of pipette has been found to have an error of rather less than ±0.1%. 5 ml of the *p*-aminodimethylaniline reagent is added immediately and the shaken mixture is allowed to stand for 4 min. 3 ml of the ferric ammonium sulphate solution is added and a Kjeldahl stopper is inserted into the neck of the boiling tube. The tube is immersed, to within 5 cm of the top, in vigorously boiling water for 50 min and then cooled in running water.

The resulting brown solution is extracted twice with 10 ml of iso-amyl alcohol and the combined organic layers are extracted twice with 10 ml of the ammonia/ammonium chloride reagent. Filtration of the separated alcohol solution through No. 1 Whatman paper produces a clear blue solution with a slight red fluorescence.

The colour is measured against a reagent blank (prepared by the same procedure except that 1.1 *N* hydrochloric acid is substituted for the hydrolysate) using an Ilford filter 626.

ACKNOWLEDGEMENT

I thank the Directors of A.R. Davis & Co. for permission to publish this paper.

SUMMARY

The considerable background colour in previous methods for the absorptiometric determination of cystine by means of *p*-aminodimethylaniline has been almost eliminated by solvent extraction of the required coloured compound. Alkali treatment of the extract intensifies the colour. The improved test is two and a half times more sensitive than previous tests based on the same reaction and the colour produced has a more sharply defined absorption peak. Cystine (plus cysteine) in protein hydrolysates may be determined with an error of less than 1%.

RÉSUMÉ

Les auteurs proposent d'effectuer une extraction à l'aide d'un solvant organique, lors du dosage absorptiométrique de la cystine au moyen de la *p*-aminodiméthylaniline. Cette modification permet d'améliorer considérablement la sensibilité de la méthode.

ZUSAMMENFASSUNG

Es wird eine Verbesserung der absorptiometrischen Methode zur Bestimmung von Cystin mit *p*-Aminodimethylanilin beschrieben. Durch Extraktion mit einem Lösungsmittel wird die Empfindlichkeit der Methode wesentlich erhöht.

REFERENCES

[1] R. FLEMING, *Biochem. J.*, 24 (1930) 965.
[2] B. VASSEL, *J. Biol. Chem.*, 140 (1941) 323.
[3] D. K. MECHAM, *J. Biol. Chem.*, 151 (1943) 643.

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CONDUCTOMETRIC AND POTENTIOMETRIC TITRATIONS OF NITROGEN BASES IN NON-AQUEOUS SOLVENTS

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INTRODUCTION

Nitrogen bases are in general determined quantitatively by titration in acidic solvents, the end-point being found either by the potentiometric method or by means of a colour indicator. In the former method solvents containing glacial acetic acid are commonly used[1], the inert balance being a compound such as benzene, chlorobenzene, chloroform or a similar solvent. The use of completely inert solvents is restricted to the colour indicator method, because the input impedance of most potentiometers is too low for such poorly conducting systems.

The main disadvantage of acetic acid is its levelling effect on the strength of nitrogen bases and its small potential range. A consequence of the latter fact is that strong and weak nitrogen bases cannot be clearly distinguished from each other. Hence, in recent years efforts have been made to find more suitable solvents with a stronger differentiating capacity. Acetonitrile[2] and methyl isobutyl ketone[3] have been among the solvents used; their potential range is 2 to 3 times that of acetic acid. Methyl isobutyl ketone as well as acetone[4] can also be used for differentiating between acids of different strength.

The disadvantage of the use of solvents with keto groups for the titration of nitrogen bases is the possibility of a reaction between primary amines and the solvent to yield ketimines ($R_1R_2C = NR_3$), which results in low values in the determinations.

The purpose of the present investigation was therefore to develop other wide-range solvents which do not react with the solutes or titrants employed. The search for these media was stimulated by the results obtained in the conductometric titration of dibasic acids, where the influence of factors like solvents, temperature, etc. was studied[5]. By analogy, the stress in the present work was laid on the determination of bivalent nitrogen bases, and the corresponding factors were considered, *viz.*: (1) The properties of the solvent, in particular: a. the solvating power (presence of groups forming hydrogen bonds, such as –OH), b. the mean dielectric constant. (2) The dimensions of the acid anions, ClO_4^- *versus* Cl^-. (3) The distance between the basic groups and steric hindrance. (4) The temperature.

EXPERIMENTAL

Solvents and titrant solutions

The solvents generally used were methanol, propanol-2, nitrobenzene and binary mixtures of these with each other or with a hydrocarbon (benzene or *n*-heptane). All solvents were chemical grade and no special purification was applied. The water content was 0.3% or lower.

The titrant solutions were 0.1 *N* perchloric and hydrochloric acid in dioxan. These reagents were prepared in the usual way, *i.e.* by dilution of concentrated aqueous solutions with the organic solvent to the required strength. The dioxan was purified by drying on solid potassium hydroxide, followed by distillation over sodium.

Apparatus

(a) The conductometric titrations were performed with the aid of the a.c. Wheatstone bridge described previously[5]. The working frequency was 1000 c/s. The electrode system was a Philips dipping cell GM 4221, consisting of platinized platinum electrodes, with a cell constant of approx. 0.8.

(b) For the potentiometric determinations either the Electrofact Precision Laboratory pH/mV meter, type 6 C 30/2/KF or the Vibron Electrometer, model 33 B (Electronic Instruments Ltd.) was employed. The input impedance of the latter instrument is much higher than that of the Electrofact meter, $10^{13}\,\Omega$ as compared with $10^{8}\,\Omega$. Hence the Vibron meter is especially suitable for poorly conducting solutions for which the Electrofact meter cannot be applied.

For all potentiometric titrations a glass–calomel electrode system was used, the latter electrode being filled with a saturated solution of potassium chloride in propanol-2. The glass electrodes were the Electrofact type 6 C 30/75, for use with the Electrofact meter, and the Beckman type 1190-90, for the Vibron meter.

It should be noted that although the absolute potential values indicated by the different combinations, millivoltmeter–glass electrode, were different, the potential range covered was, as a first approximation, independent of the type of the meter or of the glass electrodes.

The titrations were performed in a cylindrical, jacketed glass vessel closed by a cork plug. This plug was provided with holes for the electrodes, a thermometer and the burette tip. Water from a thermostat circulating through the cell jacket permitted temperature control to ± 0.05° at all temperatures used (25°, 50° and 75°). During titration the solution was stirred with a magnetic stirrer.

Titration procedure

For every titration 10 ml of a 0.01 *M* standard solution of the base was pipetted into the cell and diluted to a volume of 40–60 ml. The solution was stirred until it had attained the temperature of the thermostatted vessel. Small portions of titrant were added (approx. 0.10 ml from a semimicro burette) and the readings were taken when they became constant. This was normally the case within half a minute.

TITRATION OF MONOVALENT BASES

The monovalent bases studied belonged to various groups, *viz.* aliphatic amines, anilines and heterocyclic basic nitrogen compounds.

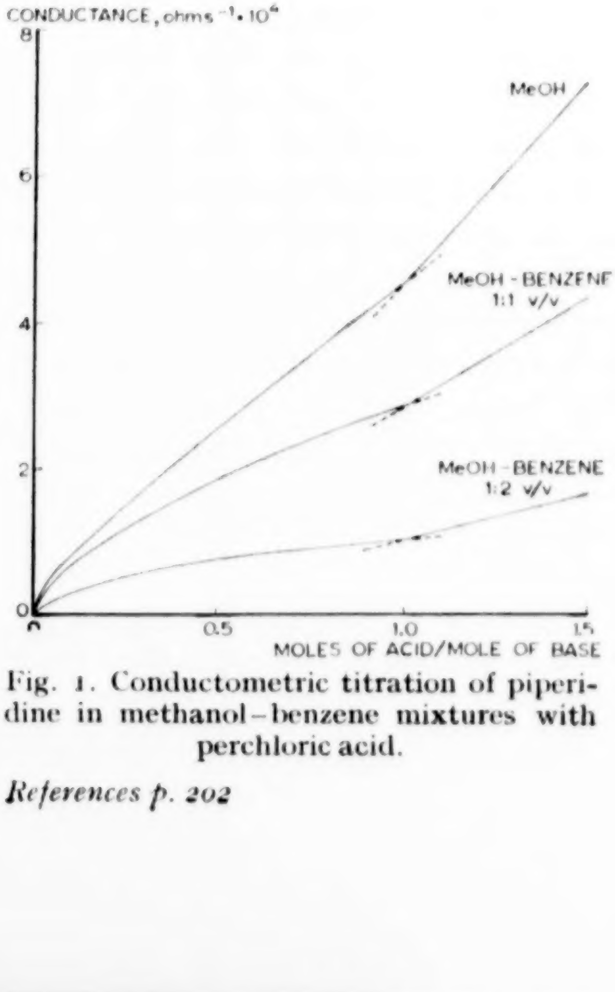

Fig. 1. Conductometric titration of piperidine in methanol–benzene mixtures with perchloric acid.

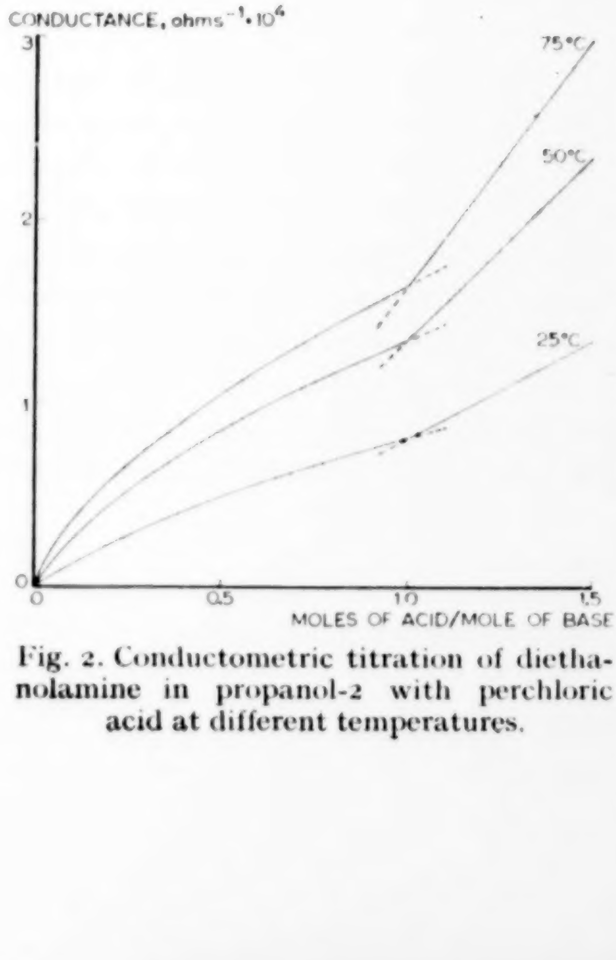

Fig. 2. Conductometric titration of diethanolamine in propanol-2 with perchloric acid at different temperatures.

In the conductometric titrations all monovalent bases gave similar curves when the same solvent was used. Consequently, a mixture of monovalent bases of different basicity cannot be differentiated in this way.

Increasing the volume fractions of hydrocarbon in the solvent methanol–benzene did not improve the sharpness of the equivalence point (Fig. 1), in contrast to raising the temperature (Fig. 2). Solvent mixtures mainly consisting of an indifferent compound such as nitrobenzene (to increase the conductance) and a small amount of methanol were unsuitable for conductometric titrations.

In the potentiometric titrations, however, this solvent system gave attractive titration curves. Optimum results were obtained both in pure nitrobenzene and in mixtures containing equal volume fractions of this solvent and dioxan or a hydrocarbon (see Fig. 4). Other solvents giving satisfactory curves were: methanol, ethanol, propanol-2 and mixtures of these alcohols with benzene (Fig. 3). From Fig. 3 it can be seen that the potential range increases in the order: propanol-2 < ethanol < methanol. (This order is valid both for the pure alcohols and for the alcohol–benzene mixtures.)

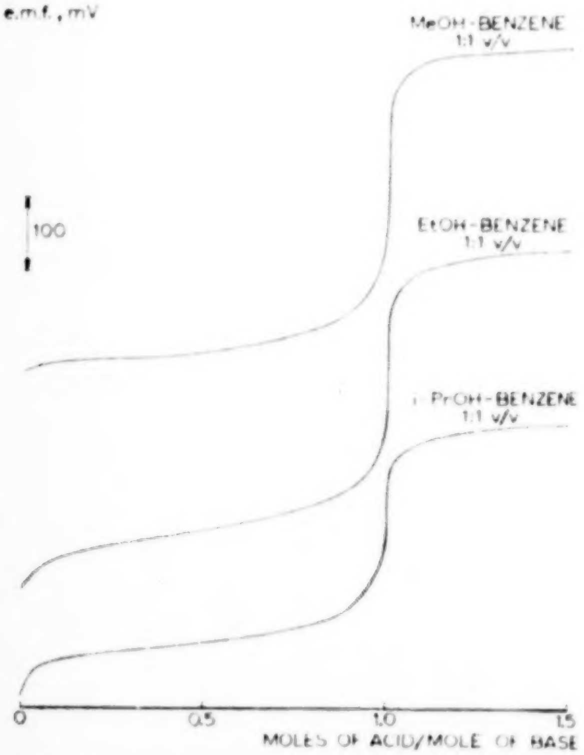

Fig. 3. Potentiometric titration of piperidine in different solvents with hydrochloric acid (curves have been shifted vertically for clarity).

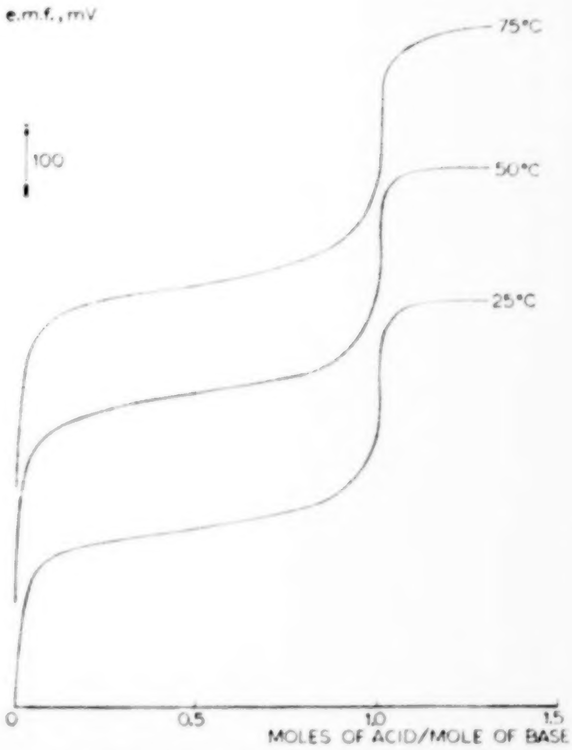

Fig. 4. Potentiometric titration of *p*-toluidine in nitrobenzene–xylene (1 : 1 v/v) with perchloric acid at different temperatures (curves have been shifted vertically for clarity).

Finally, the influence of temperature on the potentiometric titration of *p*-toluidine is shown in Fig. 4. The only effect is a possible small increase in the difference between half-neutralization potential (h.n.p.) and the final potential, *viz.* from approx. 300 mV at 25° to 350 mV at 75°.

TITRATION OF BIVALENT BASES

All the bivalent bases studied were either aliphatic or alicyclic, *viz.* members of the series of the *α,ω*-diamines and derivatives, and two diaminocyclohexanes.

With these bases special attention was paid to the four factors mentioned in the introduction, *viz.* properties of solvent, dimensions of acid anion, distance between the basic groups and temperature.

In this section we shall take the conductometric and the potentiometric titrations together and discuss the results in connection with the above-mentioned factors. Their influence is best illustrated by the experiments with the a,ω-diamines, including their derivatives.

Influence of solvent

For the solvents used the same restriction had to be made as for monovalent bases: nitrobenzene was in general unsuitable for the conductometric titrations and only alcohol–hydrocarbon mixtures were used. In potentiometry, on the other hand, solvent systems containing nitrobenzene gave the best results, just as with the monovalent bases.

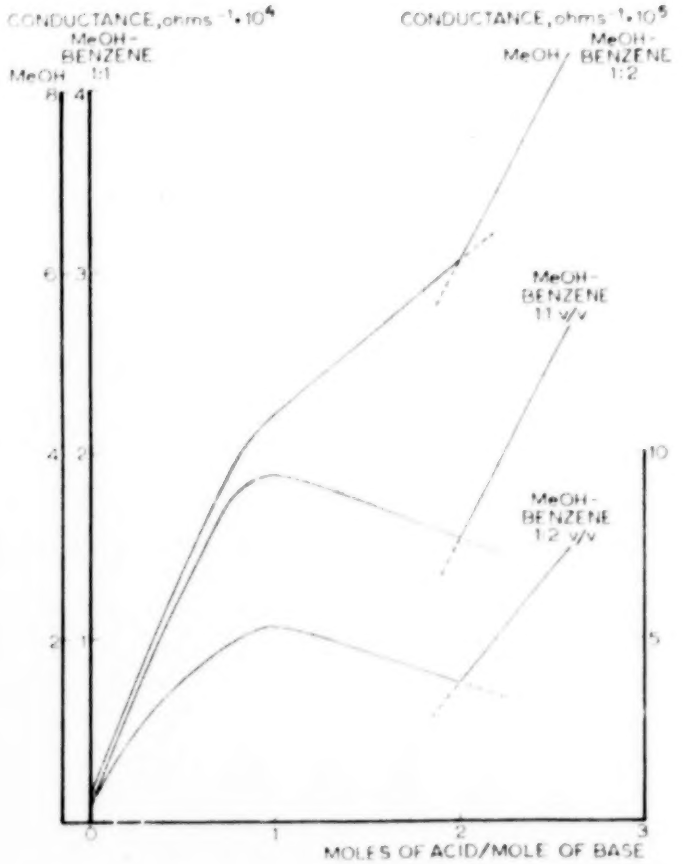

Fig. 5. Conductometric titration of ethylenediamine with perchloric acid in methanol–benzene mixtures.

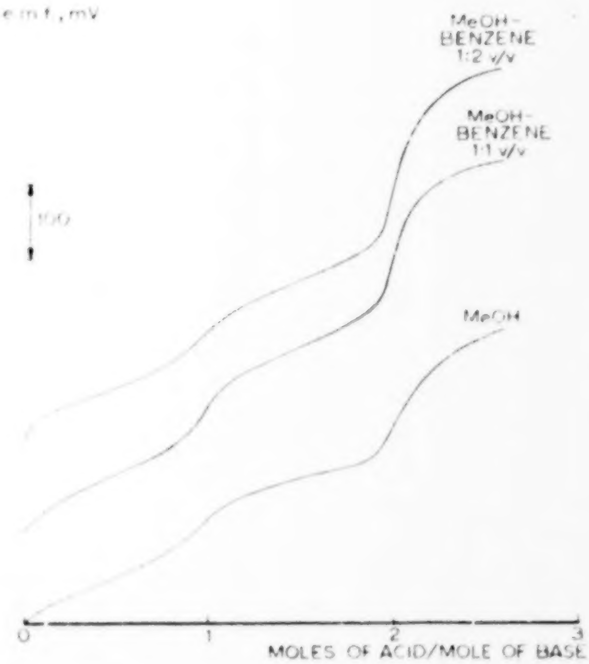

Fig. 6. Potentiometric titration of ethylenediamine with perchloric acid in methanol–benzene mixtures (curves have been shifted vertically for clarity).

Decreasing the dielectric constant, ε, of the solvent gave analogous results in conductometric titrations as previously reported for the dibasic acids[5]. The lower diamines showed more pronounced N-shaped titration curves (Fig. 5). In contrast to the results obtained with the dibasic acids the first equivalence point of the titration of bivalent amines could not be accurately determined in many cases. Consequently, application of conductometric analysis to mixtures of these compounds is somewhat restricted.

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The influence of the dielectric constant on the shape of the curves was less pronounced in the potentiometric than in the conductometric titration (*cf.* Figs. 5 and 6). In general, the first potentiometric equivalence points in solvents containing methanol are also indistinct.

In the system methanol–benzene both the dielectric constant and the mean solvating power decrease when more benzene is used. Hence the ε effect and the solvation effect reinforce each other's influence on the properties of the solvent blend, but the former predominates[5].

From the foregoing it can be seen that, although resolution of the two equivalence points is better in methanol–benzene mixtures than in the traditionally used glacial acid, the former are not ideal.

Better results are obtained when the solvating power of the solvent is considerably decreased. The results of this modification are visible in both techniques, but most clearly so for the potentiometric titrations in solvents containing nitrobenzene. An illustration of the influence of the solvating power (at approximately constant dielectric constant) on the shape of the titration curve and hence on the resolving power of the solvent is given in Fig. 7. Here the curves have been slightly displaced, so that the second h.n.p. values coincide, but since the actual h.n.p.'s did not differ by more than 25 mV, this figure represents the true titration curves very satisfactorily.

From this result we see that:

a. The upper (acidic) limit of the potentials in nitrobenzene is rather sensitive to the presence of methanol (and other strongly solvating solvents). The influence of the alcohol, however, is not as great as observed by VAN DER HEIJDE[6] in the case of pyridine.

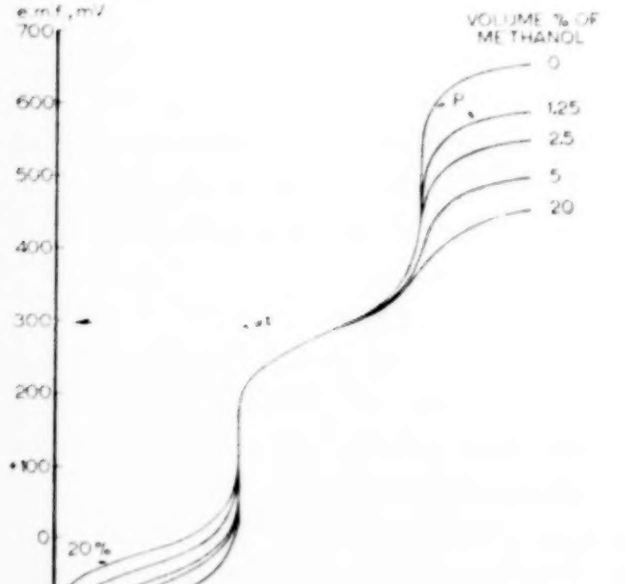

Fig. 7. Potentiometric titration of N, N, N', N'-tetramethylethylenediamine in methanol–nitrobenzene mixtures with perchloric acid (p = precipitate formation).

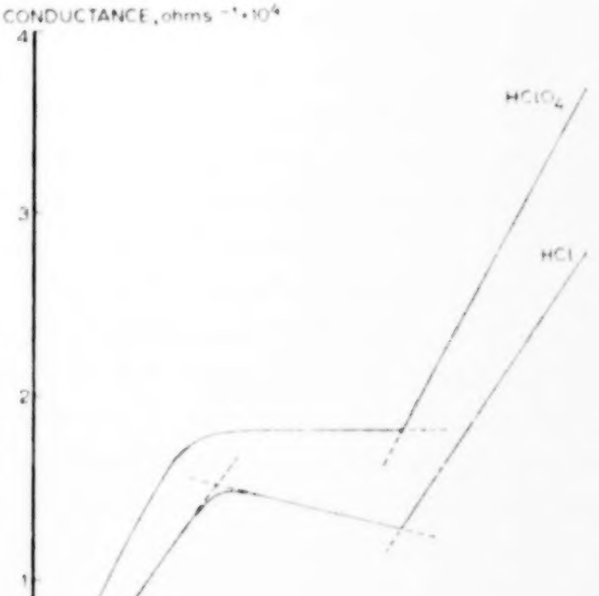

Fig. 8. Conductometric titration of ethylenediamine in methanol–propanol-2 (1 : 1 v/v) with perchloric and hydrochloric acid.

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b. the lower (basic) limit is less sensitive to the solvent composition, but it shows a pronounced decrease at very low methanol content (below 5%). The fact that the value of the second h.n.p. is nearly constant has probably no fundamental significance.
c. the difference between the first and the second h.n.p. increases with decreasing solvating power.

Dimension of acid anion

Most titrations were carried out with perchloric acid, but hydrochloric acid was used in a few cases in order to study the influence of the acid anion more closely.

From a theoretical standpoint widely different results might be expected when $HClO_4$ is replaced by HCl (the radii of the anions being 2.6 and 1.8 Å, respectively[7]), but in practice the difference between the curves is not pronounced.

In the potentiometric titrations the curves are, apart from a slight shift, practically identical, and even the difference in the h.n.p. values of the two equivalence points is almost equal: approx. 190 mV when HCl, and about 200 mV when $HClO_4$ is used.

In the conductometric curves there is a larger difference (Fig. 8) and when hydrochloric acid is the titrant it is possible to determine the first equivalence point with fair accuracy, which cannot be done when perchloric acid is used.

As mentioned above methanolic solvent systems are not ideal for these titrations (especially not for the potentiometric ones) but, when hydrochloric acid is used, methanol must be employed, as most chlorides are insoluble in solvents with lower solvating power.

Influence of distance between the basic groups

The titration of diamines having different numbers of methylene groups between the two nitrogen atoms gave, in general, curves which could be predicted from the results obtained with the dibasic acids[5], *viz.* N-shaped conductometric titration curves for compounds such as ethylene- or trimethylenediamines and their derivatives, but no N-shaped curves for the higher members of the series of the aliphatic diamines, *e.g.* hexamethylenediamine (Fig. 9).

The shapes of the potentiometric curves are analogous to those of the conductometric ones, the ethylene- and trimethylenediamines giving two inflections, hexamethylenediamine only one—*viz.* the second—(Fig. 10). From these titration curves we may conclude that the difference between the two basicity constants is greater for ethylenediamine than for the substituted trimethylenediamine.

A remarkable exception was found for the methylenediamine derivative (Figs. 9 and 10). In the conductometric titrations an N-shaped curve was never obtained, which is probably due to the structure of this compound. In the potentiometric determinations, however, two inflections are observed, both in solvating and non-solvating media (methanol and nitrobenzene). It may be supposed that the basic groups influence each other inductively through the methylene group.

The influence of steric effects is demonstrated by the behaviour of two cyclohexanediamines, *viz.* a (technical) 1,3- and a (technical) 1,4 isomer. Both compounds give an N-shaped titration curve in suitable solvents. For the former compound it is less pronounced than for 1,3-diaminopropane and its derivatives (*cf.* Figs. 9 and 11).

In the case of 1,4-diaminocyclohexane the N-shape is still less pronounced. The explanation of these phenomena will be given elsewhere.

In the potentiometric titrations the steric influence is of the same order: nitrobenzene is the only solvent in which two distinct inflections are observed, while, as a result of the factors outlined above, the distance between the two h.n.p. values is smaller for both diaminocyclohexanes than for the 1,3-diaminopropane compound.

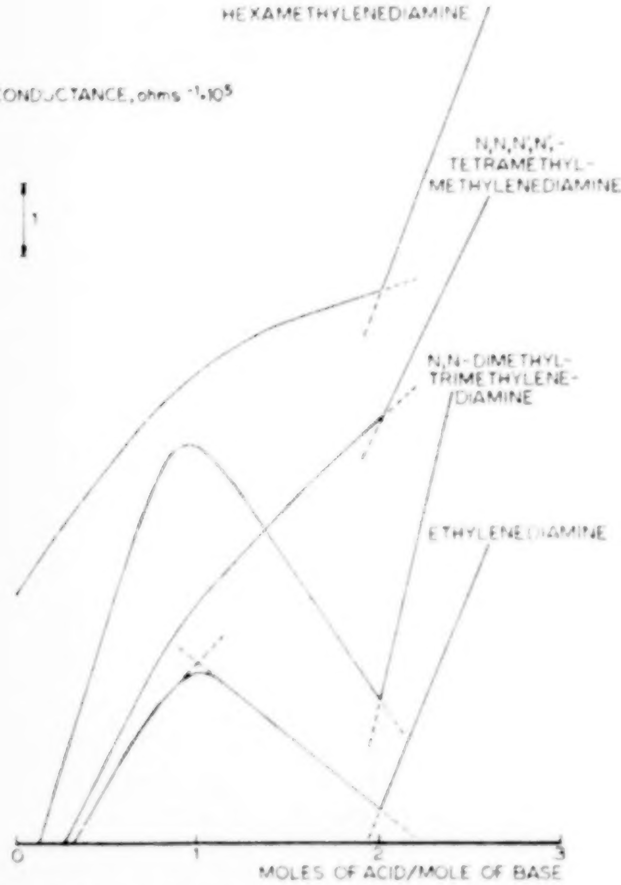

Fig. 9. Conductometric titration of diamines of different chain length in propanol-2 with perchloric acid (curves have been shifted vertically for clarity).

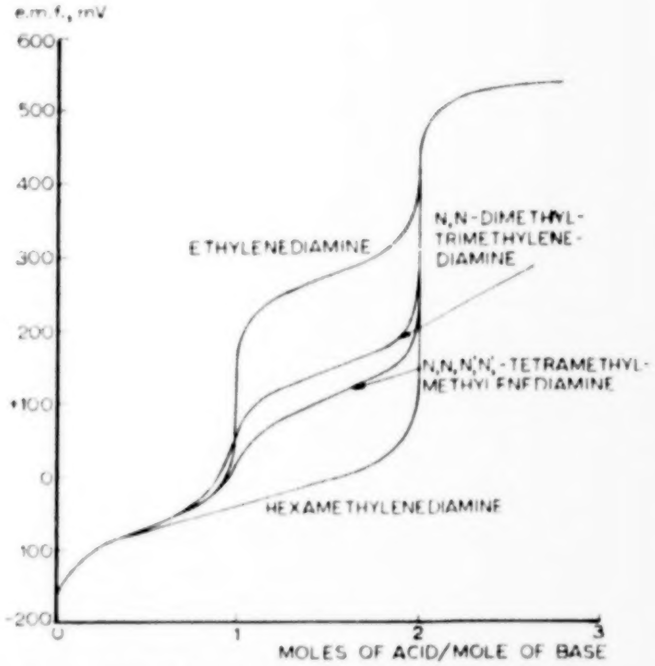

Fig. 10. Potentiometric titration of diamines of different chain length in nitrobenzene containing 2.5% v/v methanol with perchloric acid.

Influence of temperature

In the potentiometric titrations the effect of temperature is hardly noticeable; the distance between the two half-neutralization potentials is in general constant within the experimental error (10–20 mV).

The results of the conductometric titrations are completely analogous to those obtained for the dibasic acids[5], in that at elevated temperature the N-shape of the curve is more pronounced than at room temperature (Fig. 12). No exceptions to this rule have been observed. In these titrations a complication arises, however, when at higher temperatures mixtures of an alcohol and a hydrocarbon are used as solvents. Then, contrary to what is usually observed, the conductance of the solutions may decrease when the temperature is raised (Fig. 13). At the same time it is seen that the apparent sharpness of the N-curve diminishes. The explanation of these phenomena, which depend on the composition of the solvent mixture, will be given

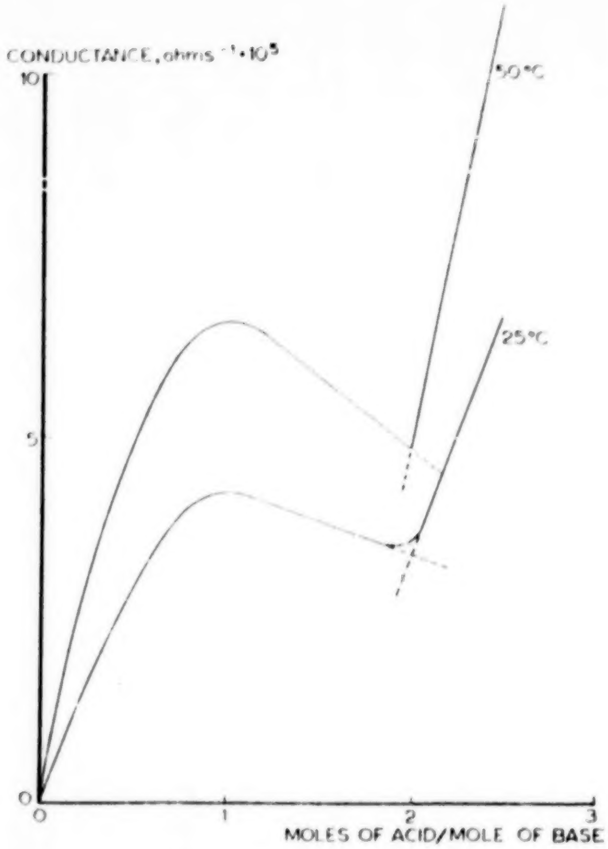

Fig. 11. Conductometric titration of 1,3-diaminocyclohexane in propanol-2 with perchloric acid at different temperatures.

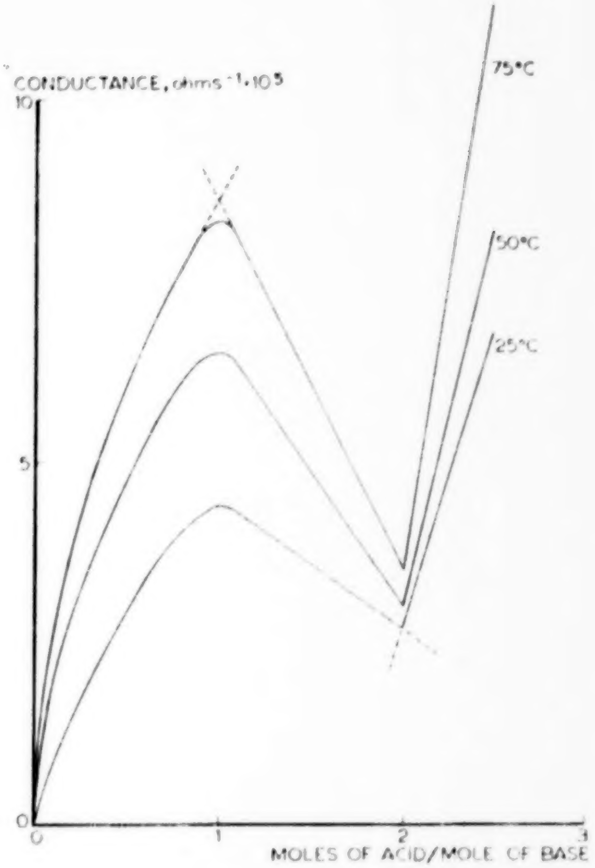

Fig. 12. Conductometric titration of ethylenediamine in propanol-2 with perchloric acid at different temperatures.

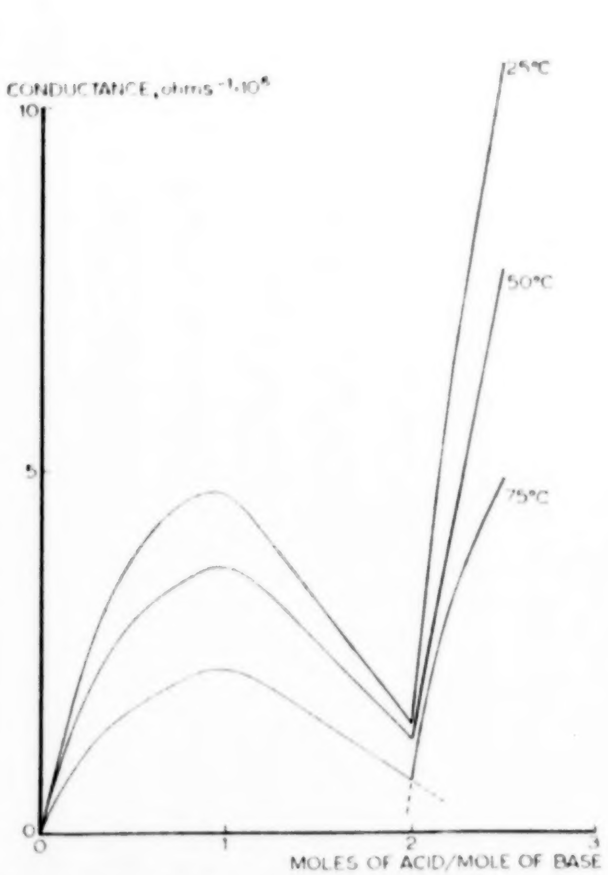

Fig. 13. Conductometric titration of ethylenediamine in propanol-2–benzene (1 : 1 v/v) with perchloric acid at different temperatures.

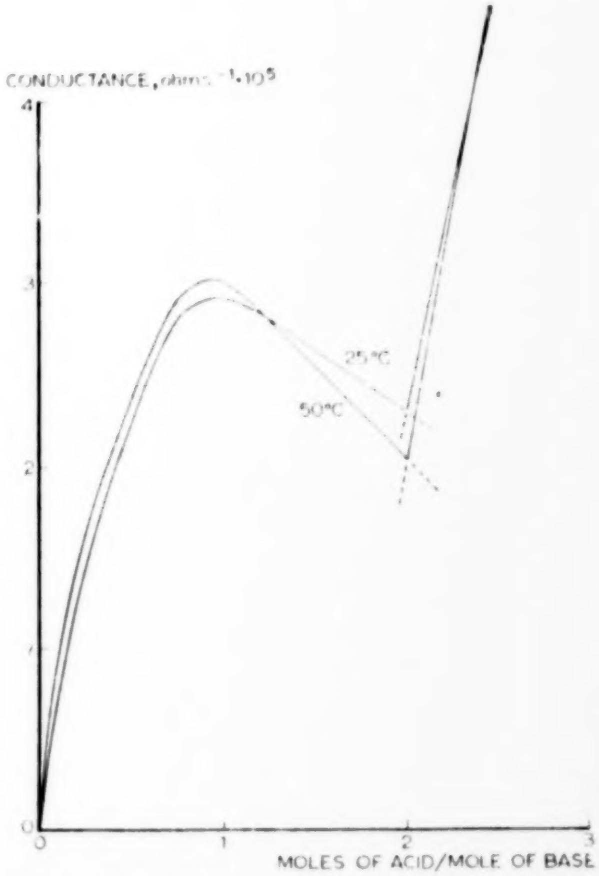

Fig. 14. Conductometric titration of ethylenediamine in ethanol–benzene (5 : 7 v/v) with perchloric acid at different temperatures.

elsewhere. If the conditions are chosen such that the conductance at 25° is approximately equal to that at 50°, the N-shaped titration curve becomes visibly sharper again (Fig. 14) just as above.

TITRATION OF MIXTURES

From the foregoing it is clear that the potentiometric method is the more favourable one for differentiating titrations. As an example the titration of a mixture of three bases in nitrobenzene with perchloric acid is shown in Fig. 15. The addition of non-polar solvents to the nitrobenzene results in curves of the same general type (*cf.* Fig. 4). In other solvents the differentiation is less clear, as can be seen from Figs. 3, 6 and 7. Hence nitrobenzene, either pure or diluted with non-polar solvents, is by far the most suitable for the titration of mixtures of organic bases*.

The application of conductometric titrations to the analysis of mixtures of bases is restricted to a few cases, in particular mixtures of a monovalent and a bivalent amine (ethylenediamine). This titration is illustrated in Fig. 16 from which it is seen that a rise in temperature results in a better determination of the first equivalence point (diethanolamine + half of the ethylenediamine) and hence in a more accurate analysis.

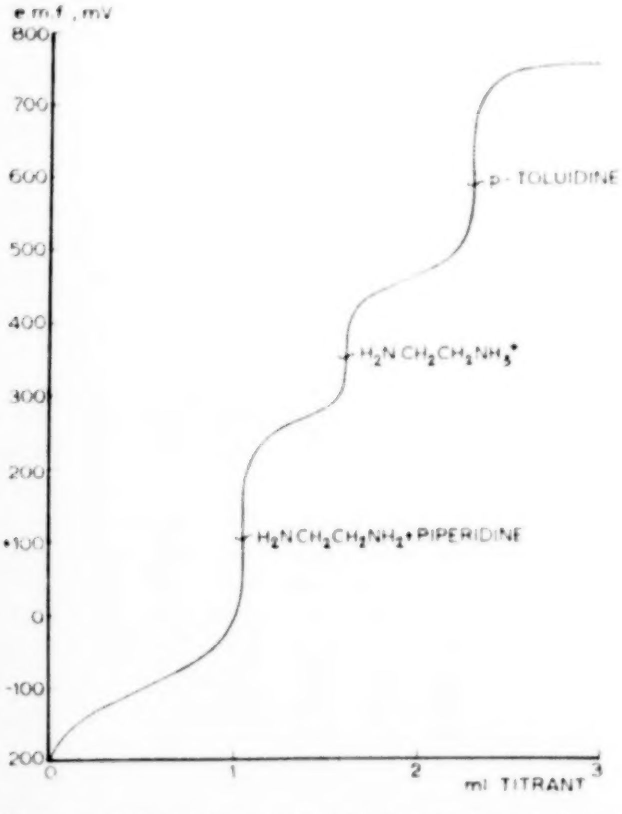

Fig. 15. Potentiometric titration of a mixture of piperidine, ethylenediamine and *p*-toluidine in nitrobenzene with perchloric acid.

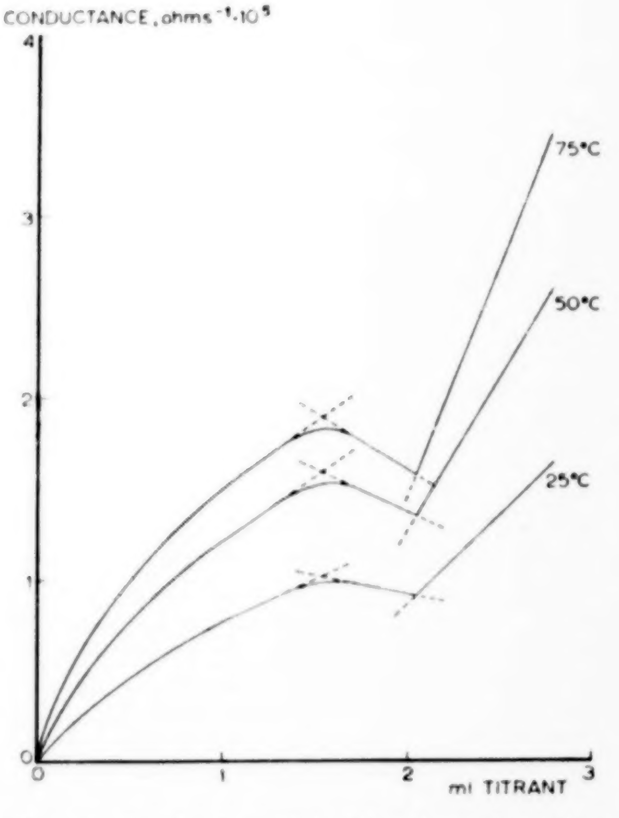

Fig. 16. Conductometric titration of a mixture of diethanolamine and ethylenediamine in propanol-2 with perchloric acid at different temperatures.

CONCLUSIONS

From our experiments we can draw the following conclusions:

1. The factors affecting the shape of the conductometric titration curve are the

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* For the potentiometric titration of acids, especially dibasic ones, nitrobenzene is less suitable than pyridine, owing to the low solubility of these compounds in non-solvating media.

same for bivalent bases as for dibasic acids, *viz.* solvent, titrant, distance between the functional groups in the solute molecule and temperature.

2. To determine basic compounds in non-aqueous media the potentiometric procedure is better than the conductometric one, especially when one is dealing with mixtures.

3. A chemically inert medium having a low solvating power but sufficient conductivity is the most suitable for these titrations. An example of this type of solvent for potentiometric titration is nitrobenzene.

ACKNOWLEDGEMENT

The authors are much indebted to Miss A. SNIP, who skilfully carried out many of the titrations. They wish to express their gratitude to Dr. Ir. P. N. DEGENS, Jr. for his stimulating interest in this investigation.

SUMMARY

This paper describes an experimental study of the conductometric and potentiometric titrations of nitrogen bases in non-aqeous media. It is shown that for bivalent bases the factors governing the shape of the titration curve are the same as those previously found for dibasic acids, *viz.* solvent, acid anion, temperature, and distance between basic groups. With the aid of this knowledge a new indifferent solvent system for potentiometric titrations has been developed, which is very attractive for the analysis of mixtures of bases.

RÉSUMÉ

Les auteurs ont effectué une étude expérimentale des titrages conductométriques et potentiométriques de bases organiques en solvants non-aqueux. Les résultats obtenus montrent que la méthode potentiométrique convient particulièrement bien à l'analyse de mélanges de bases.

ZUSAMMENFASSUNG

Es wird über ein konduktometrisches und potentiometrisches Titrationsverfahren zur Bestimmung organischer Basen in nicht-wässrigem Medium berichtet. Die erhaltenen Ergebnisse zeigen, dass die potentiometrische Methode sich besonders gut zur Analyse von Basen-Gemischen eignet.

REFERENCES

[1] J. S. FRITZ, *Acid–Base Titrations in Non-aqueous Solvents*, The G. Frederick Smith Chemical Cy., Columbus, Ohio, 1952.
[2] J. S. FRITZ, *Anal. Chem.*, 25 (1953) 407.
[3] D. B. BRUSS AND G. E. A. WYLD, *Anal. Chem.*, 29 (1957) 232.
[4] J. S. FRITZ AND S. S. YAMAMURA, *Anal. Chem.*, 29 (1957) 1079.
[5] N. VAN MEURS AND E. A. M. F. DAHMEN, 21 (1959) 10.
[6] H. B. VAN DER HEIJDE AND E. A. M. F. DAHMEN, *Anal. Chim. Acta*, 16 (1957) 378.
[7] L. PAULING, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, 1940, p. 240.

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REVUES DE LIVRE

Gaz Chromatographie 1958, Edité par D. H. DESTY, Butterworths Scientific Publications, London, 70 s., by post 2s.3 d. extra; Academic Press Inc., New York, 383 pages, $ 13.00.

En mai 1958 s'est tenu un Symposium au ,,Royal Tropical Institut'' d'Amsterdam, sous les auspices du groupe de recherches de l'Institut du pétrole et de l'Association des chimistes néerlandais, ayant pour objet la chromatographie gazeuse. Cette méthode relativement récente a pris un développement considérable car elle offre des possibilités étonnantes de séparation et elle permet, du même coup, le dosage des constituants étudiés avec une bonne précision. La rapidité n'est pas l'une des moindres qualités de processus. Les derniers progrès de la ,,gaz chromatography'' ont été présentés à ce Symposium et les exposés réunis en un volume fort bien venu et édité, dans un temps record, par D. H. DESTY. Cet ouvrage est richement illustré de graphiques, de dessins et de photographies, chaque sujet est suivi des références bibliographiques qui s'y rapportent et d'un résumé de la discussion à laquelle il a donné lieu.

L'ouvrage comprend trois sections d'égale importance. La première traite des diverses bases théoriques de la chromatographie gazeuse, dont nous citerons, par exemple, l'efficience des colonnes en ce qui concerne la forme et le remplissage, les isothermes d'absorption et le comportement chromatographique des vapeurs, la diffusion, la détermination des coefficients d'activité à dilution infinie, la chromatographie des gaz fortement radioactifs, . . .; la seconde partie a pour objet la technique et l'appareillage; on y trouve une foule de données pratiques fort précieuses pour les spécialistes: les divers processus de détections, la construction des colonnes à grande efficience pour la séparation des hydrocarbures, l'utilisation des colonnes multiples . . . Enfin, la dernière section est réservée aux exposés traitant plus spécialement des applications tels que l'automation, la séparation et le dosage des halogènes volatils, l'analyse des huiles essentielles, la séparation des dérivés d'acides aminés, l'utilisation du sucre comme phase stationnaire pour la séparation des phénols, l'application des hautes températures dans l'industrie du pétrole, etc.

La présentation est parfaite, les textes sont clairs et précis. Ce livre apportera à celui qui est déjà au courant des principes de la chromatographie gazeuse des renseignements de première main sur les derniers perfectionnements et possibilités de cette élégante méthode.

D. MONNIER (Genève)

Recommended Methods for the Analysis of Trade Effluents, présentées par un Comité comprenant l',,Association of British Chemical Manufacturers'' et la ,,Society for analytical Chemistry'', publié par la ,,Society for Analytical Chemistry'' par W. Heffer & Sons Ltd, 1958, 124 pp.

Les eaux usées rejetées par l'industrie contribuent toujours davantage à polluer lacs et rivières. C'est pourquoi, dans la plupart des pays, les gouvernements ont promulgué des lois sévères pour tenter de ralentir ce phénomène. Ceci implique un contrôle minutieux des eaux et provoque aussi des contestations et des procès. Il s'agit donc d'établir des méthodes d'analyses présentant une absolue sécurité et ce problème n'est pas aisé car les eaux résiduaires peuvent renfermer les substances les plus variées. On doit donc être reconnaissant aux analystes anglais d'avoir entrepris un telle tâche. Cet ouvrage comprend, outre la préface, 5 chapitres qui sont: Chapitre I, l'échantillonnage, Chapitre II, l'étude préliminaire de l'échantillon avec comme paragraphes principaux: la couleur, la température, le pH, la transparence, les suspensions, le résidu d'évaporation, les solides dissous, la dureté, le calcium et le magnésium. Le chapitre III traite du très important problème de la demande en oxygène, une sorte de mesure de la pollution organique; il comprend le titre en permanganate, le titre en dichromate, l'oxygène dissous, la demande biologique en oxygène. Le chapitre suivant comprend les méthodes de dosage des contaminants métalliques, Al, Sb, As, Ba, Cd, Cr, Cu, Fe, Mn, Hg, Ni, K, Se, Na, Zn . . . et le dernier chapitre des contaminants non métalliques tels que: carbone organique, chlorure, chlore résiduel, cyanure, thiocyanate, détergents synthétiques anioniques, cationiques et non ioniques, fluorure, formaldéhyde, azote combiné, phénols, phosphore et soufre combiné.

Chaque méthode y est clairement décrite de telle sorte que même des chimistes non spécialisés peuvent l'appliquer sans difficulté. Outre le principe de chaque méthode, les auteurs donnent les limites de concentrations pour lesquelles celle-ci est applicable: les réactifs utilisés, le mode opératoire et les interférences principales. On se demande pourquoi les auteurs n'ont pas donné l'erreur standard, la limite de confiance ou même simplement l'ordre de grandeur pour chaque méthode décrite.

Il n'en reste pas moins que ce livre doit être vivement recommandé car chaque méthode a été choisie et présentée avec beaucoup de soin.

D. MONNIER (Genève)

BUCHBESPRECHUNG

Chromatographische Methoden in der analytischen und präparativen anorganischen Chemie unter besönderer Berücksichtigung der Ionenaustauscher, von Ewald Blasius, 139 Abb., 40 Tab., xx + 369 Seiten, geheftet DM 96.—, ganzleinen DM 99.—; *Die Chemische Analyse*, herausgeg. von Prof. Dr. Gerhart Jander, 46. Band, Ferdinand Enke Verlag, Stuttgart, 1958.

Der Enke Verlag hat kürzlich seiner Serie „*Die Chemische Analyse*" einen neuen Band hinzugefügt, der zweifellos den Beifall der Chemiker finden wird. Es ist in der Tat sehr erfreulich, dass die deutsche Chemieliteratur nach dem Kriege solche bedeutende Werke wie das vorliegende aufweisen kann und somit auf diesem Gebiet wie bisher an erster Stelle bleibt.

Dr. E. Blasius kommt die Ehre zu, durch langwierige Arbeit sämtliche Anwendungen der Chromatographie auf dem Gebiet der analytischen und anorganischen Chemie in einem Band zusammengefasst zu haben. Das Wort Chromatographie muss hier in seinem weitesten Sinn aufgefasst werden. Wie sich dem Titel des Buches nach schliessen lässt, misst der Verfasser den Ionenaustauschern grösste Bedeutung bei.

Der Text ist klar und auch weniger erfahrenen Chemikern verständlich ohne dadurch für Fachleute an Interesse zu verlieren. Der Literaturnachweis ist reichhaltig, da Dr. E. Blasius die Veröffentlichungen bis Ende 1956 systematisch verfolgte. Ausserdem enthält das Werk einerseits eine Auswahl kürzlich erschienener Abhandlungen und andererseits zahlreiche von ihm selbst bisher nicht veröffentlichte Arbeiten.

Anschliessend gebe ich eine kurze Übersicht der Kapitel: 1. Übersicht; 2. Die physikalisch-chemische Behandlung der Probleme; 3. Das Adsorbens; 4. Das Arbeitsmedium, Wechselwirkung Ion–Lösungsmittel–Adsorbens; 5. Apparaturen für die Säulenchromatographie; 6. Verwendung von Ionenaustauschern; 7. Verwendung weiterer Adsorbentien in der Säulenchromatographie; 8. Papierstreifen oder Bögen; 9. Ionophorese auf Trägermedien, Elektrochromatographie; 10. Austauschmembranen.

Es ist zu hoffen, dass dieses ausgezeichnete Werk möglichst bald übersetzt werde, damit es Fachleuten anderer Länder zugänglich wird. Ich empfehle es wärmstens den Analytikern und diejenigen, die sich mit der anorganischen Chemie beschäftigen, in der Überzeugung, dass es für ihre Arbeit äusserst wertvolle Hinweise enthält.

I. Kapetanidis (Genève)

ANNOUNCEMENT

The Eleventh Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held at the Penn-Sheraton Hotel in Pittsburgh, Pennsylvania, U.S.A., from February 29 through March 4, 1960.

Original papers are invited on all phases of analytical chemistry, spectroscopy, and nucleonics applied to analysis. The final date for receipt of abstracts is October 15, 1959. Two abstracts should be submitted in triplicate. The first abstract should be limited to 150 words to be printed in the program. The second abstract should be of approximately 500 words to help the Program Committee evaluate and classify the paper. A letter sent with the abstracts should list the names of authors, laboratory in which the work was done, and the current addresses of the authors. All correspondence should be addressed to:

James E. Paterson, Program Chairman
The Eleventh Annual Pittsburgh Conference
Jones & Laughlin Steel Corporation
Graham Research Laboratory
Pittsburgh 30, Pennsylvania

In addition to the program of technical papers, there will be an exhibition of the newest instrumentation for analysis. More than seventy-five companies will display instruments, chemicals, and equipment.

THE USE OF SULFAMIC ACID AS A PRIMARY STANDARD IN NONAQUEOUS TITRIMETRY*

SISTER MARGUERITE MIRIAM CASO** AND MICHAEL CEFOLA

Department of Chemistry, Fordham University, New York, N.Y. (U.S.A.)

Since the choice of primary standards for use in nonaqueous titrimetry is limited, the possibility of using sulfamic acid in this field would be most acceptable. Sulfamic acid is an inorganic compound with a relatively simple structure. As a primary standard it has many advantages[1]. It is cheap, readily available, and can be easily purified from the technical grade product, from which it separates as a non-hygroscopic, white crystalline material. It is a reliable standard when used in aqueous solutions. The reagent is soluble in the basic solvents currently used in nonaqueous titrations, and work described in this paper has sought to evaluate the possibilities of using sulfamic acid as a standard in these titrations.

In 1912 FOLIN AND FLANDERS[2] extracted benzoic acid with chloroform and succeeded in titrating it in benzene. Consequently, benzoic acid quite naturally came into use for the standardization of the alkoxides and amino-ethoxides with the advent of these titrants. This acid dissolves readily in dimethyl formamide and ethylenediamine and gives reproducible titrations. It has proved unsatisfactory for titrations in butylamine, however, since the formation of a gel produces erratic results. Crystalline phenols are used in place of benzoic acid for this latter solvent. These materials form the chief primary standards in use today for the nonaqueous titrations of bases. If sulfamic acid proved a good standard in the solvent, *n*-butylamine, it could then be recommended for use in nonaqueous titrations performed in the common basic solvents. This work has succeeded in titrating sulfamic acid in all of the commonly used basic solvents by both visual and potentiometric means.

One phase of the work has shown that it is possible to titrate sulfamic acid in an acidic solvent. By conductometric means, sulfamic acid was titrated with perchloric acid in a glacial acetic acid system.

One difficulty, presenting itself at the outset of this work, was the predictable low solubility of sulfamic acid — due to its highly polar nature — in the organic solvents frequently used in nonaqueous titrimetry. This prediction was justified and sulfamic acid proved practically insoluble in dioxane, benzene, carbon tetrachloride, methanol, ethanol, isopropanol and glacial acetic acid. However, it was found that sufficient sulfamic acid dissolved in acetic acid, after refluxing the solid gently for 10 min, to give a 0.05 N solution basic to crystal violet indicator. Sulfamic acid was found to dissolve readily in the three basic solvents, dimethyl formamide, n-butylamine and ethylene-diamine, and in a fourth solvent, previously untried, dimethyl sulfoxide.

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* (a) Presented in part before the Meeting-in-Miniature of the New York Section of the American Chemical Society, March 14, 1958. (b) Based on experimental part of thesis submitted by Sr. Marguerite Miriam Caso, S.C., to the Graduate School, Fordham University, June 1958, in partial fulfillment of requirements for the degree of doctor of philosophy.

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In the very beginning of the work in nonaqueous titrations, the lack of indicators with a suitable range for acid–base titrations was realized, and titrations were first performed potentiometrically. CONANT AND HALL[3] used a chloranil indicator electrode with a calomel reference electrode for titrations in glacial acetic acid. The hydrogen–calomel pair and the antimony–antimony electrode pair were used successfully by MOSS, ELLIOTT AND HALL[4] for titrations in ethylenediamine, and these authors reported that the glass electrode did not function well in this system. FRITZ AND LISICKI[5] used the glass–antimony combination for titrations of acids in butylamine with sodium methoxide in benzene–methanol. LYKKEN[6] *et al.* reported the use of the glass–calomel system, but warned that it required constant attention in order to achieve reproducible results. Platinum electrodes have been used for titrations in tetrahydrofuran[7] and ethylenediamine[8,9]. However, diverse opinions appear in the literature on both the use of the platinum electrode and the behavior of the glass electrode in basic solvents.

Preliminary investigations for this work revealed the sensitivity of the platinum–calomel system for titrations in basic media. Reproducibility was not good when an aqueous calomel electrode was used so further experiments were made in which the calomel electrode was filled with nonaqueous solutions of either potassium chloride or lithium chloride. In using the solvent, ethylenediamine, MOSS, ELLIOTT AND HALL[4] had replaced the aqueous solution of potassium chloride with a solution of the same salt in ethylenediamine. RYAN[10], working in dimethyl formamide, had replaced the aqueous solution with a saturated solution of lithium chloride in dimethyl formamide, lithium chloride was chosen because of its increased solubility over potassium or sodium chloride in the solvent. This electrode combination proved the most promising in the preliminary investigations, so work was continued with it.

The use of indicators in basic solvents is still empirical and a study of indicators was not attempted at this stage of the investigation. Thymol blue[11] was chosen because of its accuracy in titrations involving basic solvents in general, particularly dimethyl formamide[12].

EXPERIMENTAL

Apparatus

Potentiometric titrations were performed with a Shell-Precision Dual Titrometer equipped with a sleeve-type calomel electrode and an enlarged platinum electrode. The aqueous solution of the calomel electrode was replaced by a saturated solution of lithium chloride dissolved in dimethyl formamide. The titration assembly consisted of a 150-ml tall-form beaker, covered with a plastic lid to minimize pick-up of carbon dioxide and moisture during the titration. Three holes in the lid admitted the electrodes and buret tip into the titration beaker. The titrant was delivered from a 10-ml buret calibrated at 25° in the normal way. A magnetic stirrer and a glass-covered stirring bar were used to stir the solution during the titration.

Conductometric measurements were made with the Model RC-1B Conductivity Bridge manufactured by Industrial Instruments. The cell was the dipping type platinum electrode, the plates of which were of the approximate dimensions of 12 × 13 mm, separated by a glass bead at a distance of 2 mm. The plates were platinized by electrolysis of a 3% solution of chloroplatinic acid at an applied potential of 3 V for 10 to 15 min.

References p. 214

Reagents

Sulfamic acid (Primary standard grade, Fisher), was recrystallized from water several times until it gave no opalescence with barium chloride. The reagent was dried at 105° for 3 h and its purity was assayed according to the method of BUTLER, SMITH AND AUDRIETH[1]. Potassium acid phthalate (Primary standard grade, Merck), was dried at 145° for 3 h. *n*-Butylamine (Technical, Eastman), was dried over sodium hydroxide for several days, then dried over sodium for one day and finally distilled. Dimethyl sulfoxide (Technical, Stepan), was used, as received, without further purification. Ethylenediamine (95-100%, Eastman), was further purified by the method of MOSS, ELLIOT AND HALL[4]. Dimethyl formamide (technical grade, Dupont), was purified by simple distillation.

The titrants, lithium methoxide and perchloric acid, were prepared as described below.

The concentrations of the indicator solutions, thymol blue in dimethyl formamide and azo violet in benzene, were those normally used in analytical work.

All weighings were made with calibrated brass weights and were not corrected to vacuo.

Lithium methoxide solution

To make a 0.1 *N* solution of lithium methoxide, approximately 0.6 g of freshly cut lithium metal was dissolved in 150 ml of absolute methanol, cooling the flask during the addition. When the reaction was completed, 850 ml of dried benzene were added. Sufficient methanol was added to clarify the solution, the volume of methanol being kept at a minimum[12,13]. The reagent was stored in a glass-stoppered bottle, protected from carbon dioxide and moisture.

Perchloric acid, 0.2 N

The titrant, 0.2 *N* perchloric acid, was prepared by mixing 17.0 ml of 72% perchloric acid with 200-300 ml of glacial acetic acid and adding 20 ml of acetic anhydride. The resulting solution was diluted to 1 l with glacial acetic acid and allowed to stand for at least 24 h to permit completion of the reaction between acetic anhydride and the water present[11].

Glacial acetic acid (Baker).

Benzene (anhydrous, reagent grade, Merck), was dried over sodium and distilled.

PROCEDURE

Visual titrations

Approximately 10 ml of solvent were placed in a 250-ml Erlenmeyer flask. A stirring bar was added and the solution was magnetically stirred. Three drops of thymol blue indicator solution were added and the solvent was titrated visually with 0.1 *N* lithium methoxide solution to the first appearance of a permanent, clear blue color. Less than 0.01 ml of titrant was usually required to neutralize the acidic impurities of the solvent. Approximately 0.1 g of primary standard was accurately weighed into the flask and the solution was titrated by passing 0.1 *N* lithium methoxide quickly into the flask. As the end-point was approached, one drop of base turned the solution a deep blue. The two standards, benzoic and sulfamic acids, were titrated alternately in a series of 10 determinations for each acid.

Potentiometric titrations

Exactly 0.50 mequiv. of primary standard was accurately weighed into a tall-form beaker and 10 ml of basic solvent, previously neutralized as above, were added to dissolve the sample. The beaker was mounted in the titration assembly described above and the titrant was added in small increments. The electrodes were permitted to come to equilibrium before the reading was recorded. The titration was continued several ml past the calculate end-point. The platinum-modified calomel electrode system was used for all titrations in basic solvents.

Conductometric titrations

Exactly 48.6 mg of sulfamic acid was dissolved in 40 ml of glacial acetic acid and titrated conductometrically with 0.2 *N* perchloric acid using the apparatus specified above. The same quantity of sulfamic acid was also dissolved in 40 ml of dimethyl formamide and titrated with 0.2 *N* lithium methoxide. The platinum electrode was permitted to stand in the solution for approximately 10 min to allow the system to approach equilibrium before the titration was commenced.

RESULTS

A summary of the normalities found for lithium methoxide solutions in benzene–methanol using benzoic acid and sulfamic acid is given in Table I for both visual and potentiometric titrations.

TABLE I

STANDARDIZATION OF LITHIUM METHOXIDE SOLUTIONS IN BENZENE–METHANOL

Solution A — Visual titrations Thymol Blue indicator		*Solution B — Potentiometric titrations Platinum–calomel system*	
vs. Sulfamic	*vs. Benzoic.*	*vs. Sulfamic*	*vs. Benzoic*
0.1322	0.1317	0.1031	0.1010
0.1317	0.1321	0.1029	0.1002
0.1317	0.1314	0.1020	0.0980
0.1317	0.1314	0.1000	0.0986
0.1313	0.1320	0.1016	0.0986
0.1320	0.1327	0.1027	0.1004
0.1309	0.1318	0.1020	0.1002
0.1319	0.1319	0.1018	0.1000
0.1313	0.1310	0.1020	0.1010
0.1316	0.1313	0.1014	0.1002
Av. 0.1316	0.1317	0.1020	0.0999
Std. dev. 0.00027	0.00035	0.00086	0.00091
	(parts/1000)		

As a primary standard, sulfamic acid is seen to compare favorably with benzoic acid. No precipitates or gels were evident during the course of the titration with either of these standards. Previously to this investigation, a 50-ml buret had to be used and it was noted that the 4 mequivs. of sulfamic acid needed for the larger amount of titrant produced a precipitate slightly before the end-point. This precipitate, however, did not interfere with the results and the experimental values were in agreement with the theoretical values. Cutting down the amount to 1 mequiv., and using a 10-ml buret, obviated this difficulty.

Fig. 1 shows a comparison of two electrode systems for titrations in butylamine. The platinum–calomel pair was chosen for this investigation on the basis of the sharp potentiometric break produced at the end-point. Reproducibility of results was not good with the aqueous calomel electrode because a shifting of the potential break occurred. Replacing the standard aqueous potassium chloride solution with the dimethyl formamide solution of lithium chloride enabled greater reproducibility to be obtained. Fig. 2 shows the results of titrations in dimethyl formamide using duplicate samples of sulfamic acid.

Lithium methoxide was then standardized by visual means *vs.* sulfamic acid in other solvent systems, dimethyl sulfoxide, *n*-butylamine and ethylenediamine. The results are listed in Table II. Thymol blue was used as the indicator for all the solvents except ethylenediamine. Azo violet was a better indicator for this latter solvent since thymol blue proved unsatisfactory[14]. Poorer precision with this solvent can be attributed to the predominance of benzene in the titrant, which interferes with the action of azo violet.

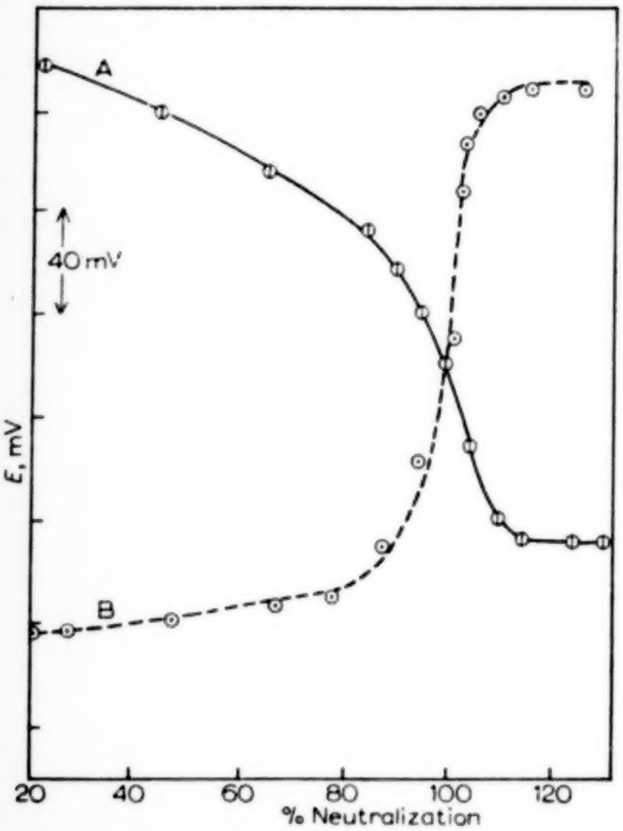

Fig. 1. Comparison of electrode systems in the solvent, *n*-butylamine. Curve A: platinum–glass electrode system. Curve B: platinum–aqueous calomel electrode system.

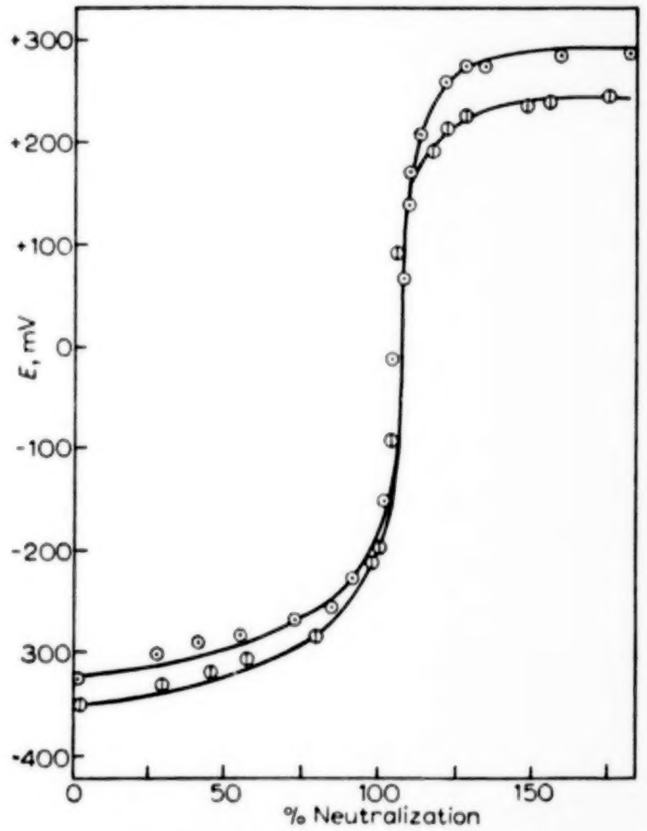

Fig. 2. Titrations in dimethyl formamide showing reproducibility of results. Electrode system: platinum-modified calomel. Solvent: dimethylformamide. Standard: 48.6 mg sulfamic acid. Titrant: 0.1031 *N* lithium methoxide.

TABLE II

NORMALITY OF LITHIUM METHOXIDE, SOLUTION A, *vs.* SULFAMIC ACID IN 4 BASIC SOLVENTS

Solvent	*Indicator*	*Determinations*	*Normality*	*Deviation from mean*	*Standard deviation (parts/1000)*
Dimethyl formamide	Thymol Blue	8	0.1316	0.00028	0.00027
Dimethyl sulfoxide	Thymol Blue	8	0.1315	0.00037	0.00039
n-Butylamine	Thymol Blue	8	0.1316	0.00029	0.00031
Ethylenediamine	Azo Violet	8	0.1315	0.00048	0.00050

A comparison of the potentiometric titrations of sulfamic acid in the four basic solvents is illustrated in Fig. 3. A large difference in the height of the potential break is evident with dimethyl formamide and dimethyl sulfoxide both of which surpass the other two. All of the solvents for this particular test were used, as received, without further purification. The solvents were simply adjusted so that they were slightly basic before titration using the neutralization method described above.

Detection of the equivalence point

A major requirement for a volumetric standard is that the equivalence point be easily detected. The method used to determine the end-point for the potentiometric titrations is shown in Fig. 4. Since the titration curve appears to be symmetrical about the end-point, the end-point can be defined by the maximal value of dE/dV. A plot of dE/dV *vs.* V can then be used to determine the precise end-point of the titration.

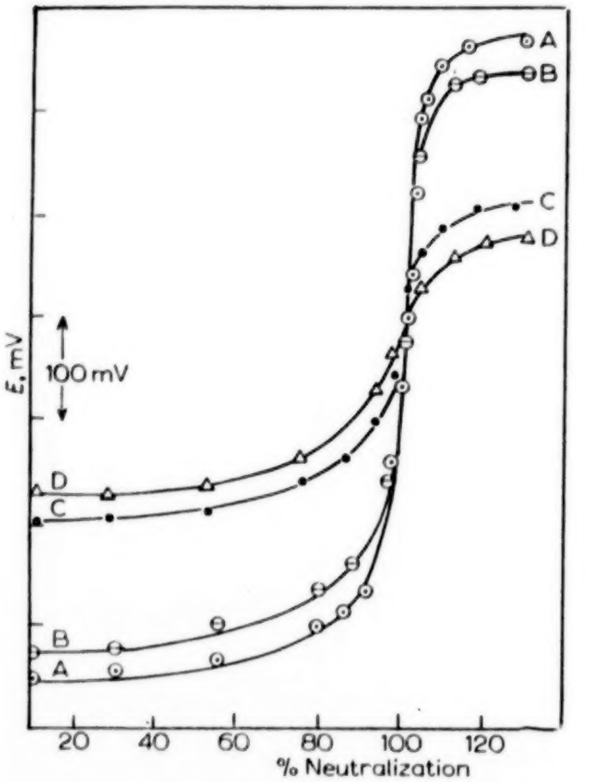

Fig. 3. Potentiometric titration of sulfamic acid in four basic solvents. Solvents: curve A — dimethyl formamide; curve B — dimethyl sulfoxide; curve C — ethylenediamine; curve D — *n*-butylamine. Standard: 48.6 mg sulfamic acid. Titrant: 0.1031 *N* lithium methoxide. Electrode system: platinum–modified calomel.

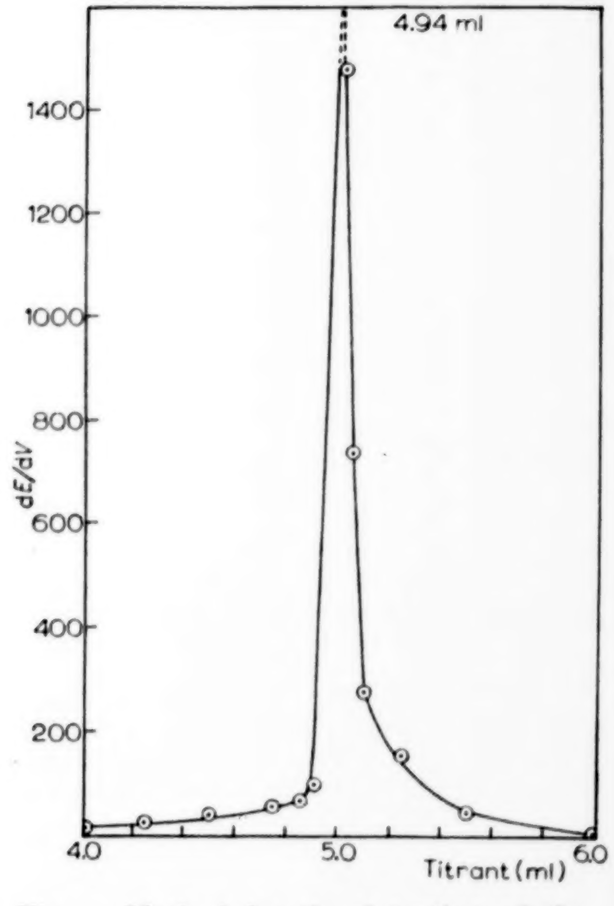

Fig. 4. Method for the detection of the end-point. Electrode system: platinum–calomel. Solvent: dimethyl formamide. Standard: 48.6 mg sulfamic acid. Titrant: 0.0998 *N* lithium methoxide.

Conductometric titrations

The titration curve for the standardization of lithium methoxide *vs.* sulfamic acid shown in Fig. 5 is interesting in so far as the conductance levels off after the end-point is reached, remaining unchanged as more titrant is added. Curves of this type were reported by MARYOTT[15] for both di-*n*-butylamine and triethylamine, however, and are apparently characteristic of anhydrous systems for titrations in basic solvents. These titrations were very tedious due to the erratic behavior of the electrodes. The reproducibility of results ranged from 3 to 9%.

Conductometric titrations proved very sensitive to changes in acidity and a sulfamic acid solution in glacial acetic acid could be titrated with perchloric acid in the same solvent. This titration curve is shown in Fig. 6. Reproducibility in acid medium was increased over that reported above and ranged from 2 to 4%.

Effect of water

The deleterious effects of water upon nonaqueous solvent titrations in general have been reported by many authors, and most basic solvents, including dimethyl formamide, have been known to be sensitive to moisture. FRITZ[16] had reported the inability of the indicator to function properly in a dimethyl formamide system when 1% of water is exceeded. A series of titrations were subsequently performed, both visually and potentiometrically, in order to determine the exact effect as the water content in the solvent was increased to 5%. The results for visual titrations are listed in Table III. Poorer precision is attributed to the slowed response of the indicator as the water content is raised. Also noticeable is the change in the normality of the titrant. Apparently this is due to the hydrolysis of the dimethyl formamide splitting off formic acid[16]. The effect of water on a potentiometric titrations is shown in Fig. 7. The steep potential break exhibited in an anhydrous system gives way to a gradual slope as the water content was raised. Also evident is the noticeable depreciation of the height of the potential break at the end-point.

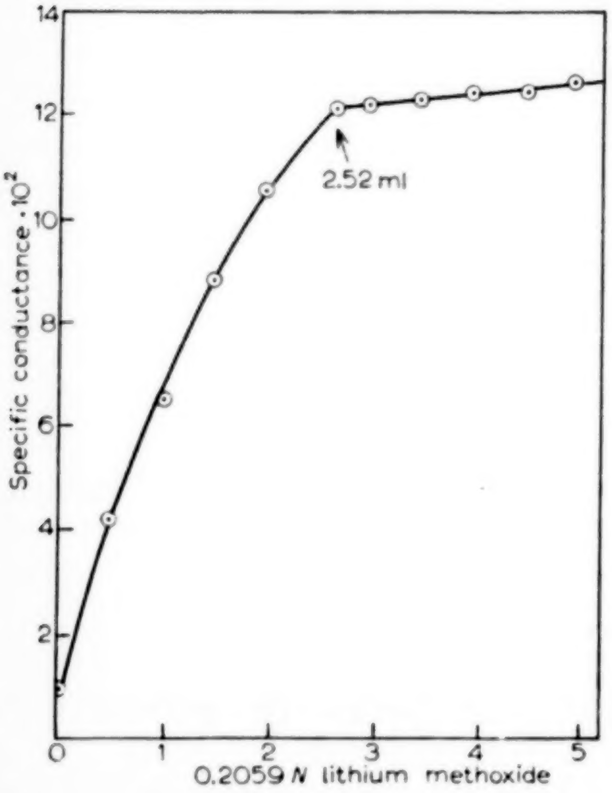

Fig. 5. Conductometric titration of sulfamic acid in dimethyl formamide. Standard: 48.6 mg sulfamic acid dissolved in 40 ml dimethyl formamide. Mequivs. sulfamic acid: calculated — 0.500, observed — 0.518.

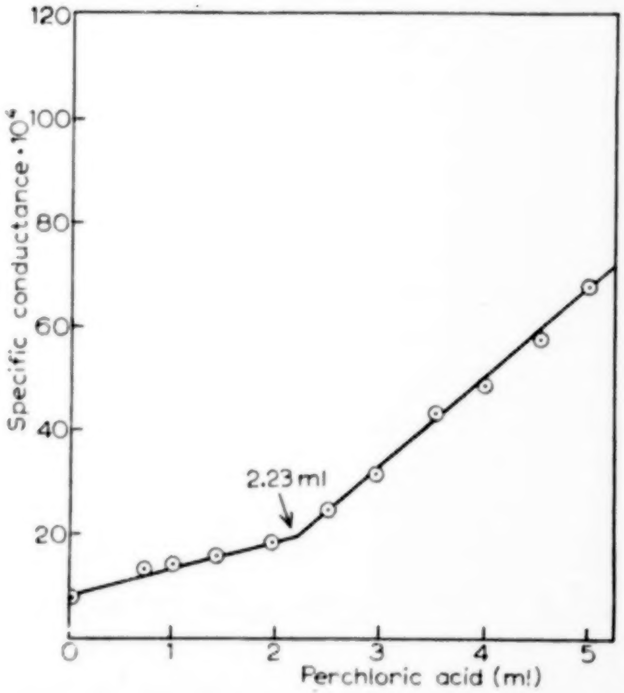

Fig. 6. Conductometric titration of sulfamic acid in glacial acetic acid. Standard: 48.6 mg sulfamic acid dissolved in 40 ml acetic acid. Titrant: 0.2250 N perchloric acid in acetic acid. Mequivs. sulfamic acid: calculated — 0.500, observed — 0.492.

TABLE III

EFFECT OF WATER UPON THE STANDARDIZATION OF 0.1 *N* LITHIUM METHOXIDE *vs.* SULFAMIC ACID

% Water	*Determinations*	*Normality, Av.*	*Standard deviation*
0	3	0.1066	0.00025
1	3	0.1067	0.00007
2	3	0.1066	0.00052
3	3	0.1061	0.00101
4	3	0.1050	0.00055
5	3	0.1053	0.00070

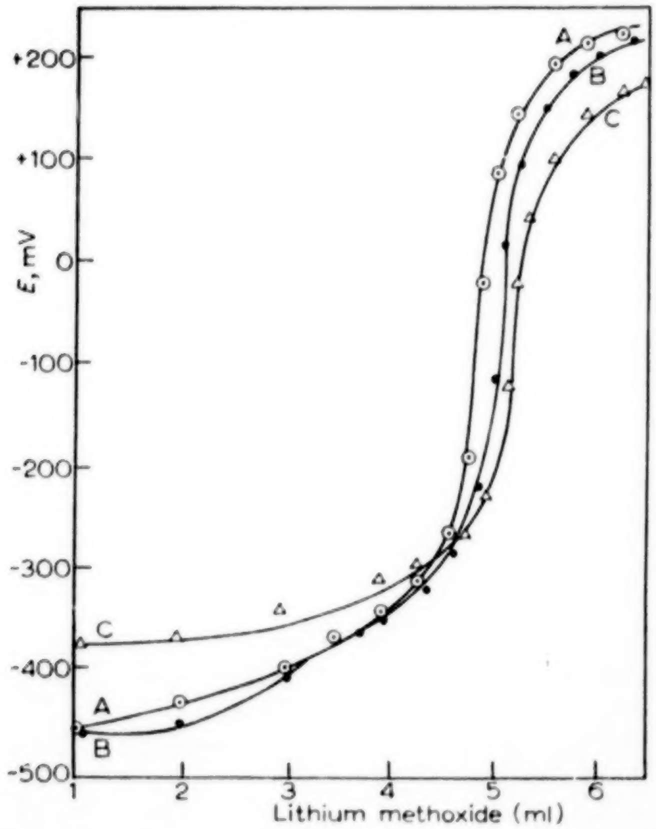

Fig. 7. Effect of increasing the water content in the solvent, dimethyl formamide. Curve A: 0% water; curve B: 2% water; curve C: 4% water. Solvent: dimethyl formamide. Standard: 48.6 mg sulfamic acid. Titrant: 0.1031 *N* lithium methoxide. Electrode system: platinum–modified calomel.

Effect of carbon dioxide

In order to ascertain the deleterious effects of carbon dioxide under ordinary laboratory conditions, visual titrations were performed after the titration solution was permitted to stand exposed to the air for intervals from 5 to 25 min. The titrations were then performed quickly, with magnetic stirring, at the close of the specified time interval, and the change in the normality of the titrant was noted. In the two series of experiments the greatest deviation up to 25 min exposure time was 5 parts per 1000, as seen in Table IV, given on the basis of deviation from the determined normality of the base.

From the results in Table IV, it seems that the rate of absorption of carbon dioxide

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TABLE IV

EFFECT OF ATMOSPHERIC CARBON DIOXIDE UPON THE STANDARDIZATION OF 0.1 *N* SOLUTIONS OF LITHIUM METHOXIDE *vs.* BENZOIC ACID

Time, min	*Determinations*	*Series A*		*Series B*	
		Normality	*Dev. Mean*	*Normality*	*Dev. Mean*
0	6	0.1082	0.0002	0.1102	0.0002
5	2	0.1081	0.0001	0.1098	0.0004
10	2	0.1081	0.0001	0.1096	0.0006
15	2	0.1084	0.0002	0.1096	0.0006
20	2	0.1081	0.0001	0.1097	0.0005
25	2	0.1088	0.0006	0.1103	0.0001

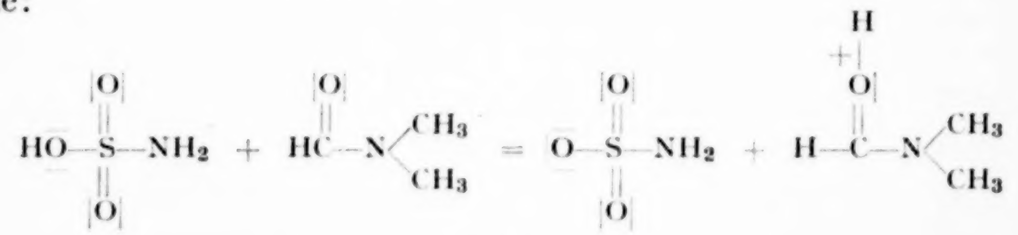
is quite slow, even under these extreme conditions. Apparently it can be concluded that dimethyl formamide can be safely used in the average laboratory with merely simple precautions taken to guard against carbon dioxide uptake.

DISCUSSION

Before performing the potentiometric titrations, the electrodes were permitted to stand in the solution for at least 10 min. It was found that this ten-minute period enabled the system to approach equilibrium and register a steady reading on the meter. The titrant was added in small increments and the electrodes again permitted to equilibrate before the reading was recorded. When this time was allowed at the start of the titrations, equlibrium was achieved within 30 to 60 sec upon the addition of each increment of titrant up to the stoichiometric point. Once this point was approached, longer intervals were required for the system to equilibrate. One of the great disadvantages of the platinum electrode can be seen here. However, the final result gave a large potentiometric break and somewhat offset this difficulty.

At first it was thought possible that the amount of water actually present in the solvent could be quantitatively estimated from the increase in the volume of titrant required for neutralization in a dimethyl formamide system. There was a definite shifting of the titration curve with the increase of water, added experimentally, but no reliable quantitative information could be established at this point in the investigation. Also, the electrode system used for these titrations approached equilibrium more slowly as the water content was increased, which made the procedure tedious. This application, in view of these difficulties, was abandoned since the Karl Fischer titration is easier to perform, either visually or potentiometrically.

The following mechanism can be proposed for titrations of sulfamic acid in dimethyl formamide:



$$\mathrm{HO{-}\overset{\overset{|\underline{O}|}{\|}}{\underset{\underset{|\overline{O}|}{\|}}{S}}{-}NH_2} + \mathrm{H\overset{\overset{|\underline{O}|}{\|}}{C}{-}N\!\!\begin{array}{l}\diagup CH_3\\ \diagdown CH_3\end{array}} = \mathrm{\overline{O}{-}\overset{\overset{|\underline{O}|}{\|}}{\underset{\underset{|\overline{O}|}{\|}}{S}}{-}NH_2} + \mathrm{H{-}\overset{\overset{\overset{H}{+|}}{O|}}{\overset{\|}{C}}{-}N\!\!\begin{array}{l}\diagup CH_3\\ \diagdown CH_3\end{array}}$$

CONCLUSION

In conclusion, the experimental behavior reported in this paper justifies the following assumptions:

1. Sulfamic acid can be titrated by both visual and potentiometric means with a

strong base, lithium methoxide, in several basic solvents. It can also be titrated with a strong acid, perchloric acid, in an acidic solvent by conductometric means, although the method is neither practical nor precise.

2. It is possible to use sulfamic acid as a primary standard in basic solvents for the standardization of lithium methoxide. When dissolved in dimethyl formamide, it standardized this base with a precision of 0.27%. Precision in other basic solvents ranged from 0.3 to 0.5%. Sulfamic acid can be used for titrations in *n*-butylamine without the formation of gels or precipitates which interfere with the titration.

ACKNOWLEDGEMENT

The authors wish to thank Doctor John C. Ryan for his helpful suggestions concerning electrode systems in basic media.

SUMMARY

A method has been developed for the standardization of a typical nonaqueous base, lithium methoxide, with an inorganic primary standard, sulfamic acid. This acid was found to dissolve readily in four independant basic solvents, dimethyl formamide, ethylenediamine, *n*-butylamine and dimethyl sulfoxide. Sulfamic acid could be titrated in each of these solvents, by both visual and potentiometric means with lithium methoxide dissolved in benzene–methanol. No gels nor precipitates resulted in the course of the titrations and the accuracy of the method was comparable to that obtained using benzoic acid as the primary standard. Conductometric titrations were also performed using sulfamic acid dissolved in two systems, dimethyl formamide and glacial acetic acid. In the latter solvent it was possible to titrate sulfamic acid with perchloric acid in glacial acetic acid.

RÉSUMÉ

Une étude a été effectuée sur le titrage d'une base non-aqueuse, le méthoxyde de lithium, au moyen d'un étalon inorganique, l'acide sulfamique. La précision obtenue par cette méthode correspond à celle du titrage au moyen de l'acide benzoïque. Des titrages conductométriques de l'acide sulfamique ont été également effectués au moyen de l'acide perchlorique dans l'acide acétique glacial.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Standardisierung einer nicht-wässrigen Base (Lithiummethoxyd) mit Sulfaminsäure als anorganischer Urtitersubstanz. Die erreichbare Genauigkeit entspricht etwa der einer Titration von Benzoesäure. Ferner werden konduktometrische Titrationen von Sulfaminsäure mit Perchlorsäure in Eisessiglösung erwähnt.

REFERENCES

[1] M. J. Butler, G. F. Smith and L. F. Audrieth, *Ind. Eng. Chem., Anal. Ed.*, 10 (1938) 690.
[2] O. Folin and F. F. Flanders, *J. Am. Chem. Soc.*, 34 (1912) 774.
[3] J. B. Conant and N. F. Hall, *J. Am. Chem. Soc.*, 49 (1927) 3047.
[4] M. L. Moss, J. H. Elliott and R. T. Hall, *Anal. Chem.*, 20 (1948) 784.
[5] J. S. Fritz and N. M. Lisicki, *Anal. Chem.*, 23 (1951) 589.
[6] L. Lykken, P. Porter, H. Ruliffson and F. Tuemmler, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 219.
[7] G. Harlow, C. Noble and G. Wyld, *Anal. Chem.*, 28 (1956) 784.
[8] G. Gran and B. Althin, *Acta Chem. Scand.*, 4 (1950) 967.
[9] M. Katz and R. Glenn, *Anal. Chem.*, 24 (1952) 1157.
[10] J. C. Ryan, *Studies in Nonaqueous Titrations*, Doctoral Dissertation, Fordham University, New York, 1956.
[11] J. S. Fritz, *Acid–Base Titrations in Nonaqueous Solvents*, The G. Frederick Smith Chemical Co., Columbus, Ohio, 1952.
[12] J. C. Ryan, L. K. Yanowski and C. W. Pifer, *J. Am. Pharm. Assoc., Sci. Ed.*, 43 (1954) 656.
[13] C. Pifer, E. Wollish and M. Schmall, *J. Am. Pharm. Assoc., Sci. Ed.*, 42 (1953) 509.
[14] J. S. Fritz, *Anal. Chem.*, 24 (1952) 674.
[15] A. A. Maryott, *J. Research Natl. Bur. Standards*, 38 (1947) 527.
[16] J. S. Fritz, *Anal. Chem.*, 24 (1952) 306.

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THE DETERMINATION OF SULPHATE IN SUPERPHOSPHATE

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INTRODUCTION

It is well known that the accuracy of the determination of sulphate by the classical technique of precipitation as barium sulphate, is dependent on the concentration and species of the various ions present in the solution. An accurate determination of the sulphate content of superphosphate, based on the quantitative collection of a chemically pure barium sulphate precipitate, would require prior removal of interfering ions and must consequently be extremely time consuming.

Furthermore, while interfering cations can be separated by cation exchange, phosphate is not readily separated without loss of sulphate. A rapid empirical method, taking cognisance of the effects of impurities contained in the barium sulphate precipitate, offers certain advantages.

EXPERIMENTAL

The method of preparing and collecting the barium sulphate precipitate was as described in text books[1,2]. In the initial stages of the experiments the precipitate was separated and collected in a sintered glass crucible and dried at 110° and in later experiments in a sintered silica crucible and ignited at 900°.

Effect of quantity of barium chloride and hydrochloric acid on the yield of the barium sulphate precipitate

It is generally known that, for a given sample composition and a given analytical procedure the amount of sulphate found will vary with the amount of excess barium chloride reagent used and with the amount of hydrochloric acid added. In order to obtain a broad picture of the effects of varying amounts of excess barium chloride reagent and hydrochloric acid present on the yield of barium sulphate, the use of an economical factorial approach seemed an automatic choice. A factorial experiment results in a considerable saving of the time and material and also estimates each main effect with the same precision.

In this experiment, a solution equivalent in composition to that of a Morocco superphosphate, but of a known sulphate content, was analysed. The solution was prepared by extracting a weighed amount of Morocco rock with hot concentrated hydrochloric acid. A measured volume of standard sulphuric acid was added and the whole was diluted to a known volume. The accuracy with which the sulphate concn. of the solution could be calculated was not perturbed by the amount of sulphate introduced with the rock because this amount was relatively small. The following levels of reagent and hydrochloric acid were used in the experiment (see Table I).

The initial volume of solution, in which precipitation was carried out, was 250 ml. After dropwise addition from a 50-ml burette, at the rate of 8 ml per min of the barium chloride reagent, each mixture was made up, with water, to the same volume of 350 ml and digested for 1 h on a steam bath. Sintered glass crucibles were used.

TABLE I

10% w/v Barium chloride reagent

Levels	*Added (ml)*	*Excess (ml)*
x_1	16	3
x_2	58	45
x_3	100	87

Hydrochloric acid

Levels	*Weight (g)*
y_1	4.563 (12.5 ml of 10 *N* HCl)
y_2	6.844 (18.75 ml of 10 *N* HCl)
y_3	9.125 (25 ml of 10 *N* HCl)

The experiment, randomized and replicated 3 times, involved 27 separate determinations of barium sulphate. The mean results of the three replicates, expressed in grams and percentage yields, are shown in Table II and Fig. 1. A result of 1.2075 g would have been quantitative.

TABLE II

YIELDS OF $BaSO_4$ FROM SIMULATED SUPERPHOSPHATE SOLUTION

Levels	x_1		x_2		x_3	
	g	%	*g*	%	*g*	%
y_1	1.20_5	99.7_7	1.21_5	100.5_5	1.21_5	100.6_1
y_2	1.21_1	100.2_6	1.22_2	101.1_8	1.22_7	101.5_8
y_3	1.20_1	99.4_0	1.22_0	101.0_2	1.22_8	101.6_7

Statistical analysis of these results showed that the excess of barium chloride and the amount of hydrochloric acid had a significant effect on the quantity of barium sulphate found. The curvilinearity of yield surface has been established by the significance of linear and quadratic effects of investigated factors in the analysis of variance. The standard deviation was found to be 0.0045 g of barium sulphate. As differences in yield equal to or in excess of 0.0082 g $BaSO_4$ become significant at the 5% level there exists a virtual horizontal plane on the yield surface, because within this area all differences in yield are less than the significant amount. In the factorial experiment this area proved to be within the limits 45–87 ml $BaCl_2$ solution and 6.84–9.13 g HCl respectively. This region is therefore one in which it is not necessary for the analyst to exercise particular care in measuring out prescribed quantities of hydrochloric acid and barium chloride solution. Quantitatively, however, this region would have overestimated sulphate content and consequently had to be abandoned in further experimentation involving use of sintered glass crucibles.

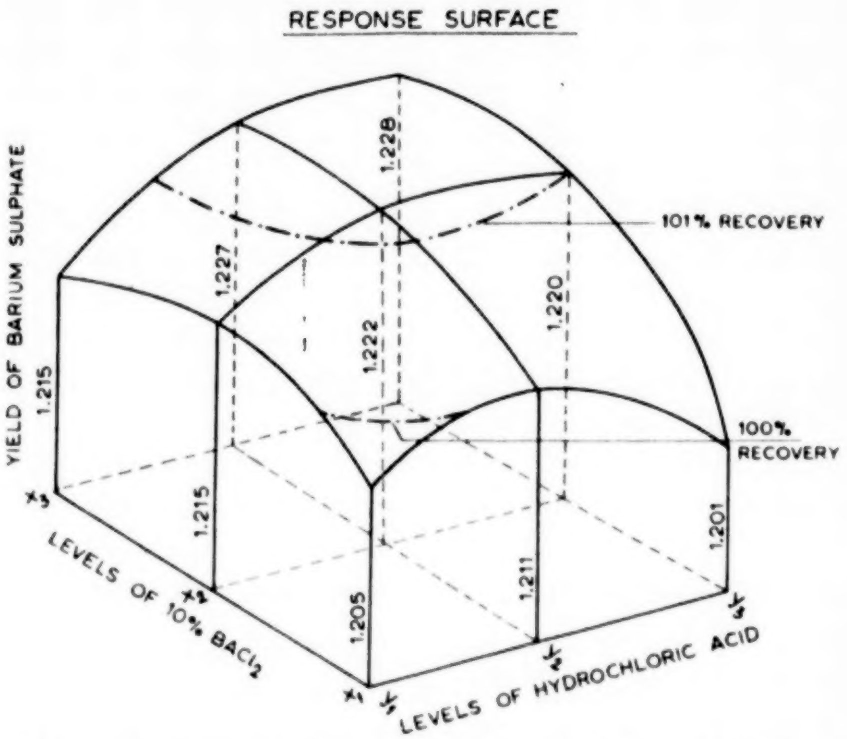

Fig. 1. Response surface (using sintered glass crucibles).

Effect of volume on precision and accuracy

The possibility existed that a greater precision could have been obtained if larger volumes of solutions had been used. This effect was therefore investigated at three levels of volume, V_1, V_2 and V_3, corresponding to 250, 450 and 650 ml respectively, prior to the addition of precipitating reagent.

The quantities of reagent are shown in Table III:

TABLE III

10% w/v Barium chloride

Levels	*Added (ml)*	*excess (ml)*
x_1	16	3
x_2	58	45

Hydrochloric acid

Levels	*N*	*Abs. weight (g)*		
		V_1	*V_2*	*V_3*
y_1	0.50	4.562	8.212	11.862
y_2	0.75	6.844	12.319	17.794

Mean yields of barium sulphate in grams and corresponding percentages are given in Table IV. A quantitative yield would have been 1.2105 g.

TABLE IV

MEAN YIELDS OF 3 DETERMINATIONS OF BARIUM SULPHATE AT VARYING VOLUMES OF SOLUTION OF SUPERPHOSPHATE

Levels	V_1		V_2		V_3	
	g	%	g	%	g	%
y_1x_1	1.2006	99.18	1.1876	98.11	1.1537	95.31
y_1x_2	1.2075	99.75	1.2200	100.78	1.2220	100.95
y_2x_1	1.2055	98.59	1.1697	96.63	1.1109	91.77
y_2x_2	1.2161	100.46	1.2251	101.21	1.2165	100.50

No statistically significant differences in precision between the three volumes considered were found, but numerically the best precision was obtained for the volume of 250 ml under the conditions of this experiment.

Since the 250-ml volume also yielded the best quantitative amount of barium sulphate, it was decided to use this volume in further experiments:

Effect of sintered silica crucible and ignition temperature on accuracy and precision

It appeared that the precision could be improved by igniting the barium sulphate precipitate in a sintered silica crucible at 900°. The standard errors of barium sulphate yields obtained from simulated superphosphate, using both sintered glass and sintered silica crucibles, were therefore compared and gave the results summarized in Table V.

TABLE V

STANDARD ERROR AND ACCURACY WITH SINTERED SILICA AND SINTERED GLASS CRUCIBLES
(calculated yield = 1.2135 g of barium sulphate)

	Silica	*Glass*
Number of determinations	6	6
Standard error	0.0018 g of barium sulphate	0.0053 g of barium sulphate
Yield of barium sulphate	1.2010 g	1.2123 g
% recovery	98.97	99.90

Since the difference between the standard errors obtained by the two procedures had been found significant at the 2% level, it was concluded that the use of sintered silica crucibles has improved the precision of the analysis. Consequently, in all further experiments, sintered silica crucibles were used.

Table V reveals also that the new procedure has depressed the barium sulphate yield by 0.0125 g. The decrease in yield was found to be significant at 0.1% level and to achieve the quantitative recovery of barium sulphate the conditions of precipitation had to be altered. This can be done by reference to the yielt surface (Fig. 1) where the required set of conditions are shown by the dotted contour at 101% recovery, on the assumption that this surface also applies to the use of the ignition procedure with sintered silica. The following new levels of reagents were selected from the contours:

10% w/w barium chloride	50 ml
hydrochloric acid	6.3875 g

It must be noted that this particular set of levels, required to give a quantitative yield of barium sulphate, was one of many possible values along a contour of the yield surface. The above choice was made because it is convenient to pipette exactly 50 ml of barium chloride and because it was observed that a high level of excess reagent gave a dense precipitate, consisting of larger barium sulphate crystals than were obtained using smaller quantities of reagent. The larger crystals settled more rapidly and were consequently easier to wash.

Effects of constituents of superphosphate

Simulated superphosphate solutions of a known sulphate content were prepared as before from Morocco (M), Saafi (S) and Phalaborwa (P) rocks: These rocks were chosen because they represent a wide range of raw materials available for superphosphate manufacture. Six determinations as described in the recommended procedure, were made on each superphosphate and gave the following results:

TABLE VI

YIELDS OF BARIUM SULPHATE FROM VARIOUS SUPERPHOSPHATES

Rock	*Calculated result (g)*	*Result found (g) (Mean of 6 determinations)*	*Yield (%)*
M	1.1973	1.2004	100.26
P	1.1815	1.1806	99.92
S	1.2041	1.2036	99.95

The standard deviation was found to be 0.002 g of barium sulphate. The highest deviation observed between calculated and found, namely 0.0031 g for Morocco rock, was found not significant, since the difference must attain the value of 0.0048 g to be significant at a 5% level.

Application of method to commercial superphosphate

A sample of approximately 200 g superphosphate was crushed in a mortar to pass through a 20-mesh sieve (Gallenkamp's specification). Sixteen identical samples were taken from a sample splitter, of which 10 samples were selected randomly. The superphosphate was then analysed in duplicate as described later and gave the following results: Mean sulphate content 40.1%, Standard deviation 0.08.

RECOMMENDED PROCEDURE

Digest approximately 2.5 g of superphosphate with 25 ml of 10 *N* conc. hydrochloric acid and 125 ml of water for $1\frac{1}{2}$ h, replacing from time to time the water lost during the digestion. Cool the solution and transfer it quantitatively to a 250-ml volumetric flask. Filter the solution through a Whatman No. 40 filter paper. To exactly 100 ml of the filtrate, add 7.5 ml of conc. hydrochloric acid and 150 ml of water. Bring the solution to the boil and add dropwise from a burette at the rate of about 8 ml per min 50 ml of 10% w/v barium chloride solution, stirring at about

200 r.p.m. with a glass rod bent at one end. Digest the precipitate for 1 h on a steam bath and collect it on a sintered silica crucible.

Wash in the usual manner, dry in an oven at 110° and ignite at 900° in a muffle furnace.

DISCUSSION

The curvilinearity of equal yield contours can only be accounted for by phenomena such as occlusion, coprecipitation, post-precipitation etc. It was never the intention of the authors to fit mathematically a surface to the points observed. The required quantities of barium chloride and hydrochloric acid to give a quantitative yield were obtained by interpolation. The mathematical fitting of a barium sulphate yield surface would call for a central composite design which is fully discussed by BOX AND WILSON[3].

Additional experiments carried out on solutions, differing in volume by not more than 50 ml, showed no detectable changes in barium sulphate yields. This is encouraging to the analyst as it relaxes somewhat the analytical procedure.

It must be noted that the standard error of barium sulphate determinations are quoted in grams of barium sulphate. It is obvious that the standard error expressed in percentages is erroneous if the barium sulphate yields happen to differ amongst themselves considerably.

The importance of the accuracy and precision of the method while establishing the yield surface, cannot be too strongly emphasized, since any possible bias in the analytical work, due either to operator or to a change in the technique, can only be detected by referring back to the original yield surface.

The method is considered to be suitable for determining the percentage sulphate content of superphosphates made from raw phosphate rocks differing in silica contents as exemplified by the Morocco and Saafi (low grade Morocco) rocks used.

It is well known[1, 2] that the accuracy of the determination of sulphate by precipitation as barium sulphate is dependent on the concentrations and species of the various ions present in the solution in which precipitation is carried out.

In the case under consideration the major sources of interference in addition to those arising from the reagents will come from the calcium, silica and phosphate present in the superphosphate. Any coprecipitation of calcium sulphate will tend to give low recoveries of sulphate while coprecipitation of barium or calcium phosphate and silicate will tend to give high recoveries. Increase of acid concentration at any given volume will lead to low recoveries of sulphate since the solubilities of both calcium and barium sulphates increase with increasing acid concentration, due to the formation of bisulphate ion. The excess of chloride will tend however to compensate for this, since barium chloride is readily coprecipitated. The large excess of barium chloride will decrease the solubility of barium sulphate due to the common ion effect.

Qualitative spectrographic examination of a few of the precipitates showed the presence of calcium, phosphate and silica, while chemical examination proved the presence of chloride ion. Quantitative determination of these impurities was not undertaken. It does therefore appear fairly certain that the quantitative recovery of sulphate obtained by the suggested method is due to compensation of errors such as have been suggested above.

References p. 221

ACKNOWLEDGEMENTS

We wish to express our thanks to Dr. E. L. TIETZ for continued advice and guidance uring the course of this work, and African Explosives and Chemical Industries, imited, for their permission to publish this paper.

SUMMARY

An accurate method developed by means of a statistical approach, has been devised for the antitative determination of sulphate in superphosphate fertilizer. The method proved to be dependent of the source of raw phosphate used in the preparation of the superphosphates amined. A standard error of two parts per thousand has been obtained and it is claimed that e method is capable of determining the existence of sources of bias, if any.

RÉSUMÉ

Une méthode est proposée pour le dosage du sulfate dans des engrais superphosphatés.

ZUSAMMENFASSUNG

Beschreibung einer Bestimmungsmethode von Sulfat als Bariumsulfat in Superphosphat.

REFERENCES

A. I. VOGEL, *Quantitative Inorganic Analysis*, 2nd Ed., Longmans, London, New York and Toronto, 1951, p. 401.

I. M. KOLTHOFF AND E. B. SANDELL, *Quantitative Inorganic Analysis*, 3rd Ed., McMillan, New York, 1952, p. 322–330.

G. E. P. BOX AND K. B. WILSON, *J.R. Statistic. Soc.* (London), 1951, B. 13, p. 1–45.

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THIODIGLYCOLIC ACID AS A REAGENT FOR ZIRCONIUM

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Of the several organic precipitating reagents suggested for zirconium[1], mandelic id is by far the most useful. This reagent and several of its derivatives particularly -bromo- and *p*-chloro-mandelic acids are specific, precipitations can be effected in irly high acid concentrations and the formation of tetramandelates offers a special dvantage when handling small quantities of zirconium[2]. VENKATRAMANIAH AND AO[3] reported the use of *m*-cresoxyacetic acid for the precipitation and separation f zirconium from a considerable number of cations.

Preliminary experiments revealed that an aqueous solution of thiodiglycolic acid, OOC-CH$_2$-S-CH$_2$-COOH, gives a white precipitate when boiled with a zirconyl salt lution. This suggested a study on the utility of thiodiglycolic acid as a reagent for zirconium. In the present communication, optimum conditions are described for tl quantitative determination of zirconium by thiodiglycolic acid. The analysis is co pleted by igniting the zirconium-complex and weighing as ZrO_2. Several metal io do not interfere in the present method.

EXPERIMENTAL

Reagents

Zirconyl nitrate: Reagent grade zirconyl nitrate supplied by A. D. Mackay Inc., was used prepare its aqueous solution. The total acidity was maintained at 0.2 *N* with respect to nitric ac and the zirconium content was ascertained by the standard *m*-nitrobenzoic acid method[2].

Thiodiglycolic acid: A stock 5% solution of thiodiglycolic acid was prepared in water fron pure sample obtained from Evans Chemetics Inc.

Procedure

To an aliquot of zirconyl nitrate solution enough nitric or hydrochloric acid maintain its final acidity 0.2–0.4 *N* were added and the solution diluted to 100 r 15–20 ml of 5% thiodiglycolic acid were now added and the system heated on steam bath for about 20 min. After an hour, the precipitate was filtered throu Whatman No. 42 and washed a few times with hot water. The precipitate and wet filter paper were placed in a silica or a platinum crucible, dried, ignited, and the zirconium weighed as ZrO_2. A representative set of data is given in T

DISCUSSION

Precipitation of zirconium-thiodiglycolate carried out in presence of mineral aci of different concentrations revealed that while sulfuric acid cannot be used, hydro chloric or nitric acid can be used provided its overall normality in the systen not exceed 0.4 *N*. In the acidic medium, the precipitate is crystalline and henc to filter and wash. It was observed that the presence of 0.1 g of elements Co, Ni, Mg, Cd, Mn, Al, Pb, Ti, Be, and alkaline earths as chlorides or nitrates causes

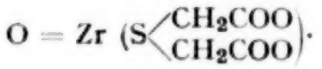
TABLE I

ZrO_2, g		
By thiodiglycolic acid	*By m-nitrobenzoic acid*	*Diff.*
0.0428	0.0429	− 0.0001
0.0514	0.0512	+ 0.0002
0.0856	0.0858	− 0.0002
0.1027	0.1024	+ 0.0003
0.1115	0.1116	− 0.0001
0.1289	0.1287	+ 0.0002
0.1540	0.1536	+ 0.0004
0.2141	0.2145	− 0.0004

interference in the present method of estimating zirconium. Although the pres of vanadyl, uranyl, iron(II) and chromium(III) gives a positive error of 0.5 when zirconium is precipitated in an aqueous medium, the error is negligib effecting the precipitation in the higher permissible acid concentration of 0.

Cerium(IV) also gives a precipitate with thiodiglycolic acid but its interference is easily avoided by reducing it initially to cerium(III) with hydrogen peroxide or thiocyanate. Thorium which is not precipitated in acidic medium tends to give high results to an extent of about 2% due presumably to coprecipitation and/or adsorption. However, by carrying out the precipitaton in 0.4 *N* nitric acid medium and using warm 0.15–0.2 *N* nitric acid as the wash liquid, it was found that the sparingly soluble zirconium thiodiglycolate can be freed completely of thorium.

An attempt was made to weigh the zirconium-complex of thiodiglycolic acid to find out its composition. The precipitate was filtered through sintered glass crucible, washed with hot water and dried at 110° for several hours. The results, within a variation of 2–5%, correspond to the formation of zirconyl thiodiglycolate:



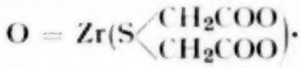
$$O = Zr\left(S\begin{array}{l}\diagup CH_2COO\\ \diagdown CH_2COO\end{array}\right).$$

Further work on the use of thioglycolic acid, iminodiacetic acid and other organic reagents for the quantitative precipitation of zirconium is in progress.

ACKNOWLEDGEMENT

We are indebted to Professor LUCY W. PICKETT and Professor PHILIP W. WEST for research facilities and interest in the work. One of us (S.B.S.) is grateful for the award of a Special Skinner Fellowship. We wish to acknowledge the gift sample of thiodiglycolic acid given by Evans Chemetics Inc., New York.

SUMMARY

Thiodiglycolic acid is shown to be a suitable precipitating reagent for zirconium. The analysis is completed by igniting the precipitate and weighing the ZrO_2. Several metal ions do not interfere. Interference due to cerium(IV) is avoided by reducing it initially to cerium(III). Estimation of zirconium can be carried out in presence of thorium. The composition of the complex is slightly variable but corresponds to zirconyl thiodiglycolate:  $O = Zr\left(S\begin{array}{l}\diagup CH_2COO\\ \diagdown CH_2COO\end{array}\right)$.

RÉSUMÉ

L'acide thioglycolique est proposé comme réactif pour le dosage gravimétrique du zirconium. Le précipité obtenu est calciné; on pèse finalement l'oxyde ZrO_2. Ce dosage peut s'effectuer en présence de thorium et de cérium.

ZUSAMMENFASSUNG

Zur gravimetrischen Bestimmung von Zirkonium kann Thioglycolsäure verwendet werden. Der gebildete Niederschlag wird zum Zirkoniumdioxyd verglüht und gewogen. Eine Störung durch Cer und Thorium kann verhindert werden.

REFERENCES

[1] F. J. WELCHER, *'Organic Analytical Reagents'*, Volumes I–IV, D. Van Nostrand Co., New York 1947.

[2] R. BELCHER AND C. L. WILSON, *New Methods in Analytical Chemistry*, Chapman & Hall, London, 1955, p. 117, 3.

[3] M. VENKATRAMANIAH AND B. S. V. R. RAO, *Anal. Chem.*, 23 (1951) 539.

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AN ULTRAVIOLET SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF VANADIUM IN ORES AND STEEL

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A spectrophotometric procedure has been developed for the determination of small amounts of vanadium in ores and steels. The method depends upon the absorption of the orthovanadate ion at 270 mμ in a 1 *N* sodium hydroxide solution. A study has been made of the ions that might interfer, and a method described for the removal of the interfering ions with an ion-exchange resin. This method avoids a number of operations described previously[1] such as repeated extraction with an organic solvent, evaporation, fusion with sodium carbonate and filtration.

Preparation of a calibration curve

A 2.0000 g sample of ammonium vanadate was dissolved in water and transferred to a 1-l volumetric flask and diluted to the mark. 10 ml of the stock solution were pipetted into a 100-ml volumetric flask and diluted to the mark with 1 *N* NaOH. 5, 4, 3 and 2 ml, respectively, of this solution were pipetted into separate 100-ml volumetric flasks which were then diluted to the mark with 1 *N* NaOH solution. The spectra of these solutions were obtained from 300 to 250 mμ on a Cary model 11 spectrophotometer using 1-cm cells and 1 *N* sodium hydroxide solution in the reference cell. The absorbance was read at 270 mμ and a Beer's Law curve was made by plotting absorbance *vs.* concn.

Determination of vanadium in ores

Transfer a 1.0000 g sample of the ore to a platinum crucible and mix with 5 g of anhydrous sodium carbonate. Spread over the mixture another 0.5 g of sodium carbonate. Fuse the mixture and allow to cool to room temperature. Transfer the crucible and contents to a 400-ml pyrex beaker and add a few ml of water. Heat to boiling in order to loosen the residue in the crucible and crush any large particles with a flattened stirring rod. Remove the crucible, wash with water and add the washings to the beaker. Add 3-5 ml of reagent grade methyl alcohol to reduce the manganate, boil for 5 min and filter hot through a filter paper (Whatman no. 42) into a small Erlenmeyer flask. Wash the residue with hot water and add the washings to the filtrate. Allow to cool, acidify to pH 2 with HCl, transfer to a 100-ml flask and dilute to the mark. Pipet 20 ml of the solution into an ion-exchange column containing amberlite IRA-400. Adjust the rate of flow of the sample through the column to approximately 30 drops per min and collect the eluate in a 100-ml volumetric flask. Rinse the column with several portions of water. Add enough NaOH solution to the flask in order to make the contents 1 M after diluting to the mark. Obtain the ultraviolet absorbance at 270 mμ on a spectrophotometer (Cary Model 11) using 1-cm cells and 1 N NaOH as reference. Read the concentration of vanadium from a standard working curve.

Determination of vanadium in steel

Weigh a 1.0000 g sample of the steel shavings into a small beaker and add 10 ml of 6 N HCl. Place the beaker on a steam bath and allow it to heat until the sample is dissolved completely. Evaporate the solution to a few ml, being careful not to evaporate to dryness, and add 2 or 3 drops of nitric acid. Heat for a few min and transfer to a 100-ml volumetric flask containing 40 ml of hot 2.5 N NaOH. The iron will precipitate and the vanadium remain in solution as sodium vanadate. After allowing the solution to cool to room temperature, dilute to the mark with water. Filter the solution or allow it to stand for a few min during which time the precipitate will settle out. Remove a 10 or 20-ml aliquot depending on the concentration of vanadium. Acidify to pH 2 or less and continue as given under the determination of vanadium in ores.

TABLE I

RESULTS OF THE DETERMINATIONS CARRIED OUT BY THE PROPOSED METHOD COMPARED TO PREVIOUSLY REPORTED VALUES ARE AS FOLLOWS:

Ore number	*% Vanadium*	
	Proposed method values	*Previously reported values*
1	0.29	0.28
	0.27	
	0.30	
	0.31	
	0.27	
2	0.19	0.19
	0.17	
	0.21	
3	0.54	0.59
	0.58	
	0.56	
	0.56	
4	0.058	0.053
	0.068	
	0.058	
5 Steel-containing chromium and vanadium	0.16	0.18
	0.16	
	0.21	
	0.19	

INTERFERING IONS

A study of the interfering elements found in ores and steel indicated that chromium was the greatest offender. Chromate ions have a strong absorption at 275 mμ and cause

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serious interference. Separation of chromate was accomplished by use of an ion-exchange resin. In concentrated acid solutions vanadium is present in the form of $(VO)_2^+$ and $(VO)^{+3}$ while the chromium is in the form of dichromate. The vanadium can be adsorbed as a cation on a cation-exchange resin or the chromium can be adsorbed as an anion on an anion-exchange resin. The latter was found to be most satisfactory for two reasons. The vanadium was difficult to elute from the cation resin and the chromate reacted with the cation resin and caused erroneous results. The procedure was tried first with standard solutions in the following manner. A standard vanadate solution was adjusted to pH 1. 20 ml of the solution was passed through an anion-exchange column consisting of Amberlite IRA-400 in the chloride form. This was followed by 50 ml of dilute HCl of the same pH. The solution and washings were collected in a 100-ml volumetric flask and made alkaline with sodium hydroxide. The ultraviolet spectrum was obtained and compared to that of a standard not passed through the column. They were identical indicating none of the ion had been adsorbed or reacted with the resin. The procedure was repeated using a solution consisting of a mixture of vanadate and chromate ions. The resulting spectrum showed absence of chromate and full recovery of the vanadium.

RESULTS

The ores used in the determinations of vanadium were of the same general type as Ore no. 1, the composition of which was as follows: Fe 67.5%; Ni 0.016%; Cr 0.004%; Mn 0.08%; SiO_2 2.40%; Al_2O_3 0.61%; MgO 0.97%; CaO 0.64%; TiO_2 0.36%; Cu 0.007%; V 0.24%.

SUMMARY

The method proposed is suitable for a quick routine determination of small amounts of vanadium in certain ores and steel. The interference of chromium in the final determination of vanadium using the ultraviolet spectra was eliminated by the use of an ion-exchange resin. Reproduceability of results was found to be acceptable for a colorimetric method.

RÉSUMÉ

Une méthode colorimétrique est proposée pour le dosage du vanadium. Elle permet un dosage rapide de cet élément dans des minerais et des aciers. Le chrome gêne; il peut être séparé par adsorption sur une résine d'échange d'ions.

ZUSAMMENFASSUNG

Es wird eine colorimetrische Schnell-Bestimmung von kleinen Mengen Vanadium in Erzen und Stahl beschrieben. Chrom, das die Bestimmung stört, kann mit einem Jonenaustauscher entfernt werden.

REFERENCE

[1] I. M. GOTTLIEB, J. F. HAZEL AND W. M. MCNABB, *Anal. Chim. Acta*, 11 (1954) 376.

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COULOMETRIC TITRATION OF +2 COPPER WITH ELECTROGENERATED +2 TIN

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The use of electrogenerated +2 tin as a coulometric titrant – especially for "coulometric iodometry" – has been described in previous papers from this laboratory[1]. The present study is concerned with the direct titration of +2 copper to the +1 state in an acidic bromide medium. Very probably +2 copper could be titrated by the coulometric iodometric technique previously described[1]. However the direct titration described herein has the advantage of greater selectivity. In principle, it is applicable to the determination of +2 copper in the presence of other oxidants, provided their oxidation potential is a few tenths of a V greater than that of the cupric–cuprous couple and provided their concentration is of the same order of magnitude (or smaller) than the copper concentration.

EXPERIMENTAL

The titration cell was the same as that depicted on p. 396, Vol. 19, (1958) of this journal, except that a platinum rather than gold generating electrode was used. The area of the platinum generator electrode was 10 cm^2 and the volume of solution titrated was 75 to 90 ml.

The supporting electrolyte was 4 M sodium bromide–0.2 M stannic chloride–0.2 N hydrochloric acid, because previous experience had shown that this composition was optimum for the generation of +2 tin with 100% current efficiency. Dissolved air was removed from the solution with nitrogen. Complete exclusion of air is required because the bromide complexes of +1 copper and +2 tin are both rapidly oxidized by dissolved oxygen.

The generating current was controlled automatically to ±0.01% by the amperostat previously decribed[2]. The generating current density can be as large as 80 mA/cm^2. It must not be smaller than about 5 mA/cm^2, because this causes the current efficiency for generation of +2 tin to fall below 100%.

Generation of +2 tin at a platinum cathode in an acidic bromide medium proceeds with practically 100% current efficiency only in virtue of the fact that the electrode acquires a film of hydrous stannic oxide which increases the overpotential required for reduction of hydrogen ion. Although this film is persistent, and is removable only by drastic solvents for hydrous stannic oxide, its effectiveness is maximal when freshly formed. Consequently the platinum cathode should be freshly cathodized in the supporting electrolyte before the sample is added. Ordinarily this is accomplished by pre-titration to the e.p. potential.

TITRATION CHARACTERISTICS

In the 4 *M* bromide solution used +2 and +4 tin very probably exist as $\mathrm{SnBr_4}^{-2}$ and $\mathrm{SnBr_6}^{-2}$, and +1 copper is present chiefly as $\mathrm{CuBr_2}^-$. The state of the +2 copper is less certain; the fact that its color is reddish brown shows that it is complexed with bromide ion, but which of the several bromo complexes predominates in a 4 *M* bromide solution is not known. Evidence discussed by KRUH[3] indicates that with about 1 *M* bromide ion the predominant species are CuBr^+ and $\mathrm{CuBr_2}$. With 4 *M* bromide ion it seems very probable that considerable concentrations of $\mathrm{CuBr_3}^-$ and $\mathrm{CuBr_4}^{-2}$ will also be present. Hence we shall indicate the +2 copper species as $\mathrm{CuBr}_n^{(2-n)+}$, and accordingly the titration reaction may be written as

$$2\mathrm{CuBr}_n^{(2-n)+} + \mathrm{SnBr_4}^{-2} + (6-2n)\mathrm{Br}^- \rightleftarrows 2\mathrm{CuBr_2}^- + \mathrm{SnBr_6}^{-2} \quad \ldots\ldots\ldots \quad (1)$$

At the temperature of 55–60° used in the titrations, and with 4 *M* bromide ion and 0.2 *M* hydrogen ion, the formal potential of the stannic–stannous couple was found to be −0.017 ± 4 V *vs.* S.C.E. (+0.201 V *vs.* N.H.E.). Under the same conditions the formal potential of the cupric–cuprous couple is +0.442 ± 7 V *vs.* S.C.E. (+0.660 V *vs.* N.H.E.). Hence the formal e.m.f. of the titration reaction is +0.459 V and its equilibrium constant (at 55–60°) is

$$K = \frac{(\mathrm{Cu}^{+1})^2\,(\mathrm{Sn}^{+4})}{(\mathrm{Cu}^{+2})^2\,(\mathrm{Sn}^{+2})} = 7 \cdot 10^{12} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

At room temperature the reaction is somewhat slow, and with either potentiometric or amperometric detection about 10 min is required for attainment of steady potential or indicator current in the immediate vicinity of the equivalence point. However at 55–60° equilibrium is reached in a few seconds prior to the e.p. and in about 2 min right at the e.p.

Fig. 1 shows the course of the potential change, and the time required to reach steady potentials after each increment of generation, in the titration at 57° of 1.59 mg of +2 copper in a volume of 100 ml. A platinum indicator electrode was used in

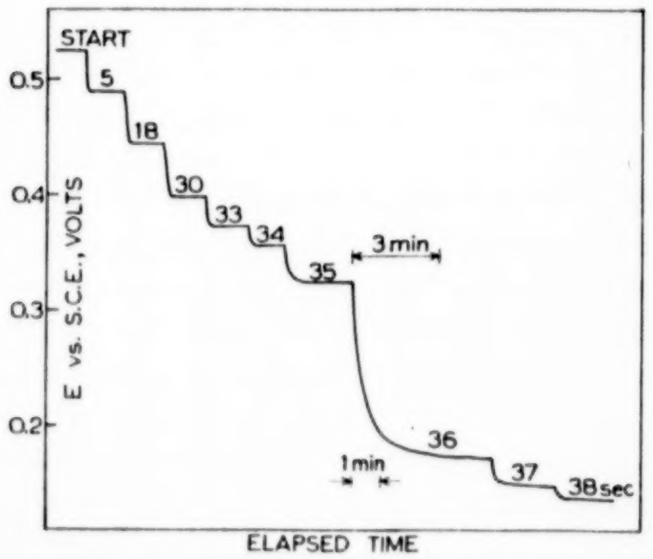

Fig. 1. Potential change of platinum indicator electrode during coulometrie titration of 1.59 mg of +2 copper at 57° with a generating current of 67.6 mA. Recorded automatically with recording potentiometer. Total elapsed time on abscissa. Numbers on each step are the cumulative generation time (sec). The theoretical e.p. time is 35.6 sec.

conjunction with a saturated calomel reference electrode. The curve was recorded with a recording potentiometer and the cumulative generation time is indicated by the number on each incremental step. The theoretical e.p. time is 35.6 sec, and up to 35 sec it is seen that the potential becomes constant almost immediately after each generation increment. At 36 sec 3 min was required for the potential to become constant to ± 2 mV, but it was within 20 mV of its final value after 1 min. The error in the e.p. time would have been only +0.05 sec if the 36 sec reading had been taken after only 1 min.

The fact that the +2 copper and +2 tin react in a 2:1 mole ratio causes the titration curve to be asymmetrical. Consequently the point of maximum slope occurs somewhat ahead of the true e.p. If no excess +4 tin were present (*i.e.*, if the titration were performed in the classical manner with a standard solution of +2 tin) the e.p. potential would be constant and independent of the quantity of +2 copper titrated. However, in the coulometric titration the fact that a large excess of +4 tin necessarily must be present causes the e.p. potential to depend on the concentration of copper titrated (*i.e.*, on the concn. of +1 copper present at the e.p.).

If no excess of +4 tin were present it follows from equation 1 that at the equivalence point $(Cu^{+2})_{e.p.} = (Sn^{+2})_{e.p.}$ and $(Cu^{+1})_{e.p.} = (Sn^{+4})_{e.p.}$ Hence from equation 2

$$\frac{(Cu^{+1})_{e.p.}}{(Cu^{+2})_{e.p.}} = \frac{(Sn^{+4})_{e.p.}}{(Sn^{+2})_{e.p.}} = K^{1/3} \qquad (3)$$

and since (at 57°)

$$E_{e.p.} = E^{\circ}_{Cu^{+2},\,Cu^{+1}} - 0.0714 \log \frac{(Cu^{+1})_{e.p.}}{(Cu^{+2})_{e.p.}}$$

and

$$\frac{0.0714}{2} \log K = E^{\circ}_{Cu^{+2},\,Cu^{+1}} - E^{\circ}_{Sn^{+4},\,Sn^{+2}}$$

the e.p. potential would correspond to any of the three relations

$$E_{e.p.} = E^{\circ}_{Cu^{+2},\,Cu^{+1}} - \frac{0.0714}{3} \log K \qquad (4)$$

$$E_{e.p.} = E^{\circ}_{Sn^{+4},\,Sn^{+2}} - \frac{0.0714}{6} \log K \qquad (5)$$

$$E_{e.p.} = \frac{E^{\circ}_{Cu^{+2},\,Cu^{+1}} + 2E^{\circ}_{Sn^{+4},\,Sn^{+2}}}{3} \qquad (6)$$

From the formal potentials of the cupric–cuprous and stannic–stannous couples quoted above the e.p. potential in this case would be +0.136 V *vs.* S.C.E.

However with stannic tin present at a constant concentration of 0.2 *M* it follows from equation 2 that at the e.p.

$$\left[\frac{(Cu^{+1})^2}{(Cu^{+2})^2\,(Sn^{+2})}\right]_{e.p.} = \frac{K}{0.2}$$

and since $(Cu^{+2})_{e.p.} = 2(Sn^{+2})_{e.p.}$ we have instead of equation 3

$$\frac{(Cu^{+1})^2_{e.p.}}{(Cu^{+2})^3_{e.p.}} = \frac{5\,K}{2} \qquad (7)$$

from which

$$(Cu^{+2})_{e.p.} = \left(\frac{2}{5}\right)^{1/3} K^{-1/3}\,(Cu^{+1})^{2/3} \qquad (8)$$

The concentration of +1 copper present at the e.p. is very nearly equal to the initial concentration of +2 copper titrated, and if we denote this concentration by C it follows as a very good approximation that instead of equation 6

$$E_{\text{e.p.}} = +0.136 - \frac{0.0714}{3}\log\frac{5}{2} - \frac{0.0714}{3}\log C \quad \ldots\ldots\ldots\ldots \quad (9)$$

or

$$E_{\text{e.p.}} = +0.127 - 0.024 \log C \quad \ldots\ldots\ldots\ldots\ldots \quad (10)$$

Thus the e.p. potential decreases by 24 mV for a ten-fold increase in the concentration of copper titrated.

These characteristics are demonstrated in Fig. 2, in which 1 is the theoretical titration curve for the classical titration without excess +4 tin present, 2 is the theoretical coulometric titration curve of $5 \cdot 10^{-3}$ M copper in 0.2 M stannic chloride–4 M sodium bromide–0.2 N hydrochloric acid, and 3 is the theoretical coulometric titration curve of $2.5 \cdot 10^{-4}$ M copper. The circles are experimental points obtained with the corresponding quantities of copper, and their good agreement with the theoretical curves is evident.

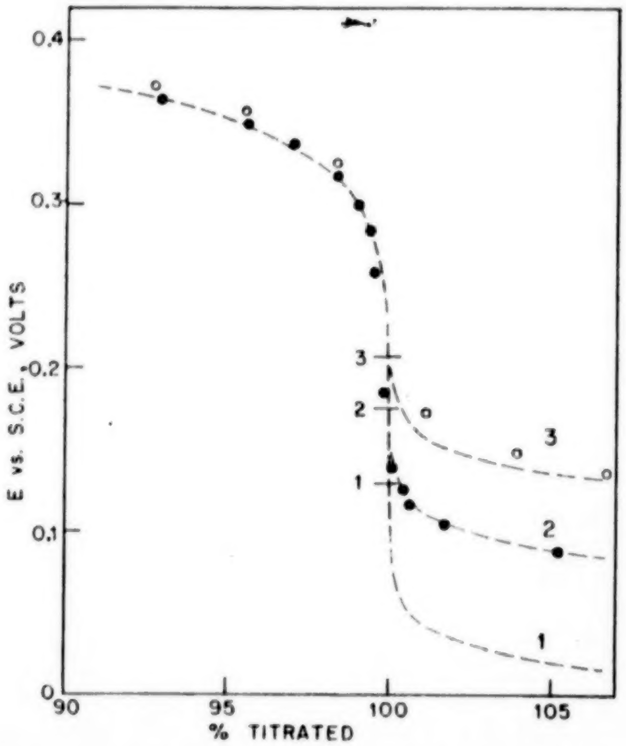

Fig. 2. Theoretical titration curves at 57°: (1) with no excess of +4 tin; (2) with 0.2 N stannic chloride and 32.6 mg of +2 copper per 100 ml; (3) as 2, except only 1.59 mg of +2 copper. The circles are experimental points with a generating current of 67.63 mA. The short horizontal bars on each curve mark the theoretical equivalence point potentials.

In practice the point of maximal slope is taken as the end-point. Under the extant conditions, and with 1 to 35 mg of copper per 100 ml, the point of maximal slope precedes the true equivalence point by 30 to 35 mV. With 1 mg of copper per 100 ml this discrepancy corresponds to a titration error of approximately −0.7%, and with 35 mg of copper per 100 ml the corresponding titration error is −0.1%. However this negative titration error is more or less compensated by the fact that the current efficiency for generation of +2 tin is 0.2 to 0.3% short of 100%, which produces a corresponding positive titration error.

Successive samples can be titrated in the same batch of supporting electrolyte, but when this is done two facts should be kept in mind. Firstly, each sample after the first must be freed from dissolved air before it is added, as otherwise some of the +1 copper already present from the previous titration will be oxidized and a positive error will result. Secondly, when in each case the point of maximal slope is taken as the e.p., a negative titration error appears, which increases with each succeeding sample, due to the circumstance that the true e.p. potential shifts progressively to a less positive (more reducing) value as +1 copper accumulates (eq. 10). The rate of potential change at the e.p., and hence the precision, also decreases in the presence of an increasing concentration of +1 copper. Consequently, if maximal accuracy is needed, no more than two or three successive samples should be titrated in the same batch of supporting electrolyte.

The end-point can also be detected amperometrically, by observing the change in current between two small platinum electrodes which are subjected to a small, constant applied voltage (50 to 150 mV). The principle of two electrode amperometry has been discussed in detail elsewhere[2]. As expected, the amperometric titration curve is V-shaped and the point of minimum current occurs very close to the equivalence point. However, amperometric detection is no more precise than potentiometric detection, and it is slower and less convenient because it requires a graphical plot. With potentiometric detection one simply titrates to the known e.p. potential.

PERFORMANCE DATA

The data in Table I demonstrate that the titration of 1.5 to 33 mg of copper in a volume of 75 to 90 ml, with potentiometric e.p. detection, can be performed with an average error of ±0.3%.

In these trials the supporting electrolyte was freed from dissolved air with nitrogen, and then adjusted (by cathodic generation) to an indicator electrode potential of

TABLE I

TITRATION OF +2 COPPER WITH ELECTROGENERATED +2 TIN

The supporting electrolyte was 4 *M* sodium bromide–0.2 *M* stannic chloride–0.2 *N* hydrochloric acid, and the volume was 75 to 90 ml. Air was removed with nitrogen. The temperature was 57 ± 2°, the generating current was 67.63 ± 1 mA, and the area of the platinum generating cathode was 10 cm^2.

Trial No.	*Cu taken mg*	*Time Sec*	*Cu found mg*	*Error mg*	*Error %*
1	1.587	35.5	1.581	−0.006	−0.4
2	1.587	35.9	1.598	+0.011	+0.7
3	1.587	35.7	1.589	+0.002	+0.1
4	1.587	35.5	1.581	−0.006	−0.4
5	1.587	35.4	1.578	−0.009	−0.6
6	3.169	71.3	3.178	+0.009	+0.3
7	6.52	146.4	6.52	0.00	0.0
8	6.52	146.7	6.53	+0.01	+0.2
9	6.52	147.1	6.55	+0.03	+0.5
10	13.01	291.7	12.99	−0.02	−0.2
11	32.63	730.4	32.55	−0.08	−0.2
12	32.63	730.9	32.57	−0.06	−0.2

0.25 ± 0.03 V *vs.* S.C.E. before the sample solution was added. The sample solution was not freed from dissolved air before it was added (except when it was added to a previously titrated solution), but a few minutes was allowed for the nitrogen stream to flush out the oxygen thus introduced before the titration was begun. The point of maximum slope of the titration curve was taken as the end-point.

In trials 3, 4, and 5 successive samples (air-free) were added to the previously titrated solution. In trial 2 the generation had been carried beyond the e.p. to obtain the data necessary for determining the point of maximum slope of the titration curve. Therefore the solution was adjusted back to the e.p. potential (point of maximum slope) by anodic generation before sample 3 was added. A similar procedure was followed in the successive trials 4 and 5. Each sample solution after the first was freed from dissolved air before it was added. Note that the titration error became progressively more negative. This happened because as +1 copper accumulated the discrepancy between the point of maximal slope (used as the end-point) and the true equivalence point increased. Although this effect will be smaller with the larger amounts of copper, these trials demonstrate the inadvisability of titrating more than two or three successive samples in the same batch of electrolyte.

Most of the elements commonly associated with copper, such as zinc, tin, lead, nickel, manganese, cobalt, aluminum, silver, and mercury, do not interfere. Ferric iron will interfere because it is reduced concomitantly with the +2 copper, but ferrous iron should not interfere.

Gold, when present in the +3 state, is titrated along with the copper and only a single e.p., corresponding accurately to the sum of the two metals, is observed. It should be possible to analyze copper–gold alloys by first determining the sum of the two metals by the present titration, and then determining the gold by coulometric titration with electrogenerated chlorocuprous ion by a method previously described[4].

SUMMARY

Using a supporting electrolyte composed of 4 *M* sodium bromide–0.2 *N* hydrochloric acid–0.2 *M* stannic chloride, and a platinum generator cathode, +2 copper can be titrated accurately to the +1 state with electrogenerated +2 tin. With potentiometric end-point detection, quantities of copper from about 1 to 35 mg in a volume of 90 ml are titratable with an error of ± 0.3%. The titration is applicable in the presence of most of the elements that are commonly associated with copper.

RÉSUMÉ

Une méthode précise est proposée pour le dosage coulométrique du cuivre(II), par réduction en cuivre(I) au moyen de l'étain(II) formé au cours du titrage. Ce dosage peut s'appliquer en présence de la plupart des éléments accompagnant généralement le cuivre.

ZUSAMMENFASSUNG

Kupfer(II) lässt sich coulometrisch mit Zinn(II) bestimmen, wobei Kupfer(I) entsteht. Die meisten anderen Elemente, die häufig mit Kupfer zusammen vorkommen, stören nicht.

REFERENCES

[1] A. J. Bard and J. J. Lingane, *Anal. Chim. Acta*, 20 (1959) 463.
[2] J. J. Lingane, *Electroanalytical Chemistry*, 2nd Ed., Interscience Publishers, Inc., New York 1958, p. 503.
[3] R. Kruh, *J. Am. Chem. Soc.*, 76 (1954) 4865.
[4] J. J. Lingane, *Anal. Chim. Acta*, 19 (1958) 394.

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VOLTAMMETRIC, POTENTIOMETRIC AND AMPEROMETRIC STUDIES WITH A ROTATED ALUMINUM WIRE ELECTRODE

III. AMPEROMETRIC DETERMINATION OF FLUORIDE WITH THE RAlE

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Examples of the anodic depolarization of the RAlE by fluoride in acid medium have been presented in previous papers[1,2]. Fluoride yields an anodic diffusion current which is proportional to its concentration. The present paper is concerned with the development of a rapid, simple, and fairly selective amperometric method for the determination of fluoride which is based on the measurement of its anodic diffusion current at a given applied potential. In a subsequent paper the use of the RAlE in the amperometric titration of fluoride with suitable cations will be described.

A few years ago BAKER AND MORRISON[3] recommended a simple cell for the rapid amperometric determination of fluoride. The cell was composed of a straight piece of aluminum wire (0.125 inch in diameter) as anode and a 10-inches long and 0.03-inch diameter platinum spiral as cathode. The cell was short-circuited, the contents stirred with a magnetic stirrer and the current measured after 2 min. The current is claimed to be proportional to the fluoride concentration. The size of the aluminum wire as stated by the authors (0.5 inch of exposed length) indicates that its surface area was several times larger than that of our RAlE[1]. The above authors observed a fairly large and fluctuating current upon short-circuiting the cell. When fluoride was added, the current increased rapidly to a maximum value, then decreased continuously with time, and became almost zero after about 80 min. The current measured after 2 min was found to be approximately proportional to the fluoride concentration. It is stated that chloride causes serious interference, phosphate and sulfide cause some, while nitrate, sulfate and cyanide do not interfere. In order to eliminate chloride interference MEGREGIAN[4] tried several electrodes other than aluminum and found zirconium suitable. In a brief note on the amperometric titration of traces of fluoride with thorium nitrate JOHANNESSON[5] used a cell composed of a rotated aluminum electrode and a stationary platinum wire electrode. The cell used by us differs in three important respects from that used by previous authors[3,4]. Firstly, the electrode is rotated at a constant speed which provides reproducible stirring conditions. Secondly, the size of the RAlE (0.15 cm^2 of exposed area) is such that exhaustion of fluoride as a result of the electrolysis is very slow and amounts to a loss of the order of 1% per 10 min electrolysis (see Fig. 2). This slow exhaustion is very important in our procedure because a time lapse of 5 to 10 min for obtaining a constant current was required (*vide infra*) after placing a "cleaned" electrode in the fluoride solution.

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Thirdly, by using the saturated calomel electrode (SCE) as a depolarized reference electrode, it was possible to select the appropriate applied potential at which no interference by chloride and many other anions is observed.

Various factors which affect the fluoride diffusion current have been studied systematically and the results are described in this paper. The recommended procedure for the amperometric determination of fluoride is independent of the reproducibility of the surface area of the electrode since the "method of standard addition" could be used[6] which is based on the proportionality between diffusion current and concentration of fluoride. It is of great practical consequence that the recommended procedure is not interfered with by relatively large concentrations of phosphate. The method has been found eminently suitable for the rapid determination of fluoride in potable and natural waters in a concentration region between 10^{-5} and $3 \cdot 10^{-4}$ *M* (0.2 to 6 p.p.m. fluoride).

EXPERIMENTAL

Materials

Sodium fluoride (Baker's analyzed) was dried at 150° and cooled in desiccator. A stock solution was prepared which contained 2.206 g of the salt per l. It was standardized gravimetrically by the lead chlorofluoride method using the procedure described by HILLEBRAND AND LUNDELL[7]. By proper dilution a 10^{-3} *M* solution was then prepared. Fluoride solutions were kept in polyethylene bottles. All other reagents were C.P. products. Conductivity water was used for the preparation of all solutions. Oxygen was removed by bubbling through 99.99% pure Linde nitrogen.

Apparatus

The electrode, electrolysis cell, etc. have been described previously[1].

Current-time curves

Such curves in fluoride solutions were determined (a) using the saturated calomel electrode (SCE) as a reference electrode without applying a potential; (b) as (a) at an applied potential of —0.75 V, and (c) using a platinum spiral (0.1 cm diameter, 2 cm in length) without applying a potential. Before each experiment the electrode was pretreated in the EDTA buffer solution as described in previous paper[1, 2]. Since fluoride induces the cathodic reduction of oxygen at the RAlE[2], measurements were made in a nitrogen atmosphere after the solution had been deareated by bubbling through nitrogen for 10 min. When the electrode was short-circuited against the SCE in a supporting electrolyte composed of 0.2 *N* acetic acid or an acetate buffer of pH 3.6, a large residual current was observed in the absence of fluoride which diminished within 5 min (curve A, Fig. 1) to a small constant value of 0.3 μA. Curve B in Fig. 1 represents the change in current with time when fluoride was added to the solution after the residual current had become constant. The fluoride current increased very rapidly and became equal to the diffusion current within 10 min. From then on the current decreased only slightly (3% in 30 min) as a result of decrease of the fluoride concentration in the solution caused by the continuous electrolysis. A similar current-time plot was obtained by applying —0.75 V (*vs.* SCE) as shown in curve A of Fig. 2. Curve B in Fig. 2 illustrates the fact that the limiting current is proportional to concentration up to a fluoride concn. of $3 \cdot 10^{-4}$ *M*. Upon the first addition of fluoride to the supporting electrolyte about 10 min were required to attain the diffusion current. After successive additions of fluoride the corresponding limiting current reached a constant value within less than 5 min. When the RAlE was short-circuited against the platinum spiral (instead of the SCE) the residual currents became larger, of the order of 1 to 1.5 μA, and less reproducible. Also the fluoride currents became less reproducible and exhibited irregular variations with time of electrolysis. The platinum spiral anode cannot be recommended as a reference electrode.

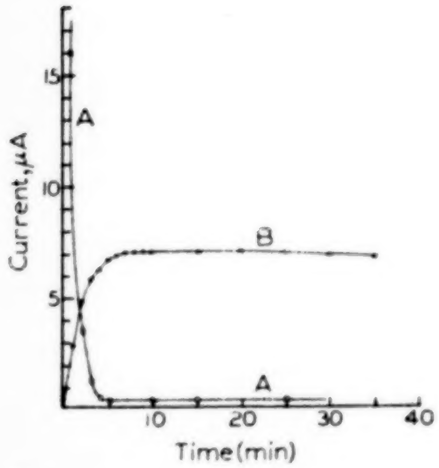

Fig. 1. Current–time curves in 0.2 N acetic acid (pH 2.80), short-circuited against SCE. (A) Residual current in absence of fluoride; (B) solution made $5.6 \cdot 10^{-5}$ M in fluoride.

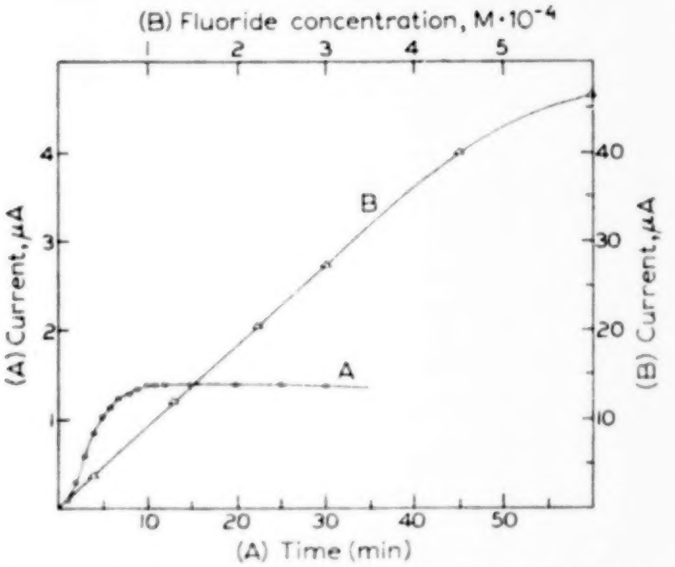

Fig. 2. Current–time curves in acetate buffer (pH 3.60) at E applied of —0.75 V. (A) $1.5 \cdot 10^{-5}$ M fluoride. (B) Proportionality between current and fluoride concentration. Lower abscissa and left hand ordinate refer to curve A.

Sensitivity of the electrode for fluoride

A diffusion current at a rotated electrode of given dimensions is proportional to the concentration of the diffusing species:

$$i_d = k\,C$$

in which C is the molar concentration in the solution. The value of k for an electrode of given surface area varies with the speed of rotation. For a given electrode at a constant rate of rotation the sensitivity may be expressed by

$$k = \frac{i_d}{C}$$

For an electrode of the usual dimensions k is expressed in μA for a millimolar solution.

In the following section is reported the reproducibility of the value of k for fluoride ions in buffers of varying pH. Also the effect of several anions on the value of k (and hence on the diffusion current of fluoride) is reported.

Effect of pH on the electrode sensitivity

After a systematic study it was decided to measure the fluoride diffusion current at an applied potential of —0.75 V (*vs.* SCE). The selection of this potential eliminates the interfering effect of such anions like chloride, bromide and perchlorate which cause depolarization when the potential of the aluminum electrode is less negative than about —0.6 V (*vs.* SCE)[1]. The residual current was measured first in the particular medium and then increasing amounts of fluoride were added and the diffusion current

TABLE I

EFFECT OF pH ON k AND ON REPRODUCIBILITY; APPLIED POTENTIAL —0.75 V *vs.* SCE

Electrolyte	*NaF concn.*	i_a *(μA)*	k $\mu A/mM/l \cdot 10^{-2}$	*Duplic.*[a]
0.1 M $HClO_4$ pH 1.1	$2.00 \cdot 10^{-5}$	3.45	1.71	1.72
$i_r = 1.50$ μA	$5.60 \cdot 10^{-5}$	9.60	1.71	1.72
	$9.00 \cdot 10^{-5}$	15.10	1.66	1.71
	$1.50 \cdot 10^{-4}$	25.30	1.70	1.71
	$3.10 \cdot 10^{-4}$	47.80	1.54	1.65
0.01 M $HClO_4$ pH 2.1	$2.00 \cdot 10^{-5}$	3.20	1.60	1.66
$i_r = 0.50$ μA	$5.60 \cdot 10^{-5}$	9.10	1.62	1.66
	$9.00 \cdot 10^{-5}$	14.50	1.61	1.63
	$1.50 \cdot 10^{-4}$	23.20	1.54	1.63
	$3.50 \cdot 10^{-4}$	48.80	1.40	
	$5.10 \cdot 10^{-4}$	58.00	1.13	1.18
Acetic acid–sodium acetate pH 3.60	$2.00 \cdot 10^{-5}$	1.98	0.99	0.97
$i_r = 0.3$ μA	$5.60 \cdot 10^{-5}$	5.60	1.00	0.96
	$9.00 \cdot 10^{-5}$	8.75	0.97	0.96
	$1.50 \cdot 10^{-4}$	14.30	0.95	0.96
	$2.30 \cdot 10^{-4}$	22.60	0.98	0.96
	$3.90 \cdot 10^{-4}$	35.10	0.89	0.85
	$5.10 \cdot 10^{-4}$	39.00	0.76	
Acetic acid–sodium acetate pH 4.60	$2.00 \cdot 10^{-5}$	1.60	0.80	0.80
$i_r = 0.25$ μA	$5.60 \cdot 10^{-5}$	4.50	0.80	0.81
	$9.00 \cdot 10^{-5}$	7.20	0.80	0.81
	$1.50 \cdot 10^{-4}$	12.25	0.81	0.81
	$3.10 \cdot 10^{-4}$	22.90	0.74	0.78
	$4.50 \cdot 10^{-4}$	32.15	0.71	0.76

[a] The duplicate determinations were not made consecutively. After running a series of experiments from pH 1.1 to 4.60 the constancy of the k value was checked by running the set in the reverse order from pH 4.60 to pH 1.1.

measured after the appropriate time (5 to 10 min). All current data reported have been corrected for the residual current. As is illustrated by Fig. 3 and in Table I, the sensitivity of the electrode reaction increases as the pH is decreased. It is interesting to note that the sensitivity in 0.1 to 0.01 N perchloric acid is about twice as great as that at pH 4.6. This result was quite unexpected considering that 10^{-4} M aluminum ions hardly interfere with the amperometric fluoride determination at a pH of 1 but very seriously at a pH of 3.6 (*vide infra*). From Table I it is noticed that the residual current increases with increasing acidity. In spite of the higher sensitivity of the electrode at lower pH it is recommended to carry out the determination of fluoride in an acetate buffer (pH 3 to 3.6) because the residual current was found much smaller and reproducible between 0.3 to 0.35 μA.

Effect of phosphate on the fluoride current

The fluoride limiting current is decreased by the presence of phosphate ions. From the analytical point it is important that small concentrations of phosphate of the order of 10^{-3} M or less have little effect. Even though the decrease in current becomes greater at higher phosphate concentrations, the proportionality between current and concentration is still maintained. The effect of phosphate is also dependent on the pH of the solution. In perchloric acid solution of pH 1.1 the value of k in the absence

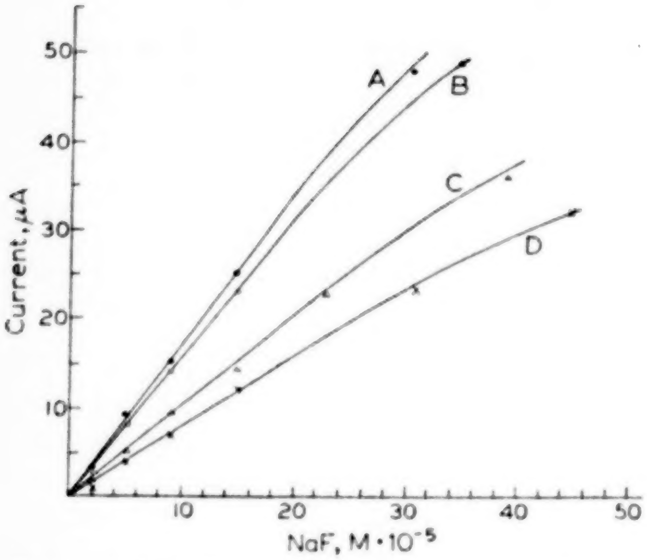

Fig. 3. Fluoride current *vs.* concentration at various pH. (A) 0.1 *M* $HClO_4$; (B) 0.01 *M* $HClO_4$; (C) acetate buffer pH 3.60; (D) acetate buffer pH 4.60.

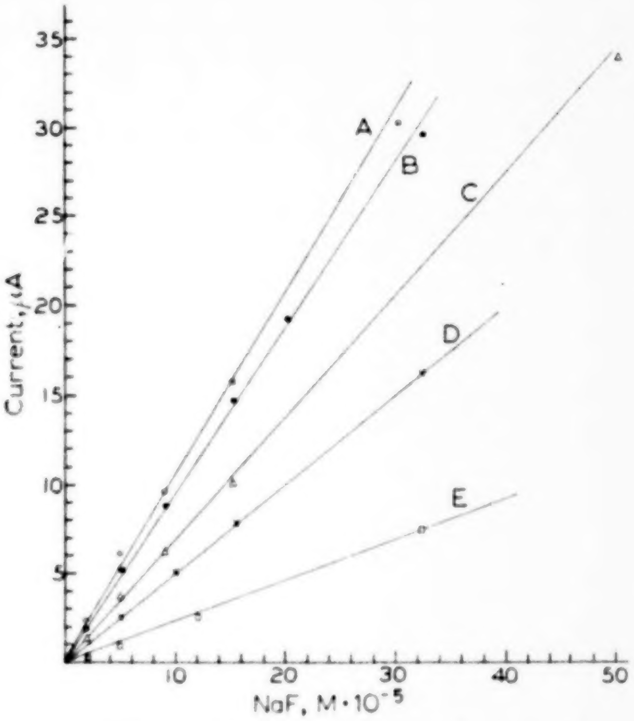

Fig. 4. Effect of $2 \cdot 10^{-3}$ *M* KH_2PO_4 at various pH. (A) 0.1 *M* $HClO_4$; (B) 0.01 *M* $HClO_4$; (C) acetate buffer pH 3.60; (D) acetate buffer pH 4.0; (E) acetate buffer pH 4.60.

of phosphate was found to be $1.7 \cdot 10^2$; $1.0 \cdot 10^2$ in the presence of 10^{-3} *M* phosphate and $0.75 \cdot 10^2$ in 0.01 *M* phosphate. At pH 2.0 these values were $1.6 \cdot 10^2$, $1.0 \cdot 10^2$ and $0.65 \cdot 10^2$; while in acetate buffer pH 3.6, they were $0.98 \cdot 10^2$, $0.70 \cdot 10^2$ and $0.55 \cdot 10^2$, respectively. The interference by phosphate greatly increases at pH 4.6; the value of the proportionality constant at this pH was found to decrease from $0.8 \cdot 10^2$ in the absence of phosphate to about $0.15 \cdot 10^2$ in the presence of $2 \cdot 10^{-3}$ *M* phosphate. Many of the data are reported in Table II. The effect of 0.002 *M* monopotassium dihydrogen phosphate on i_d at different fluoride concentrations and varying pH is illustrated in Fig. 4.

TABLE II

EFFECT OF PHOSPHATE ON THE FLUORIDE CURRENT AT VARIOUS pH; APPLIED POTENTIAL: —0.75 V *vs.* SCE

Electrolyte	*NaF concn. M*	i_d *(μA)*	i_d/C $\mu A/mM/l \cdot 10^{-2}$
	0.1 M $HClO_4$; pH 1.1		
KH_2PO_4 concn. = 0	$2.00 \cdot 10^{-5}$	3.45	1.72
$i_r = 1.50$ μA	$5.60 \cdot 10^{-5}$	9.60	1.71
	$9.00 \cdot 10^{-5}$	15.10	1.68
	$1.50 \cdot 10^{-4}$	25.30	1.69
	$3.10 \cdot 10^{-4}$	46.80	1.50
$2 \cdot 10^{-3}$ *M* KH_2PO_4	$2.00 \cdot 10^{-5}$	2.10	1.05
$i_r = 1.90$ μA	$5.60 \cdot 10^{-5}$	6.00	1.07
	$9.00 \cdot 10^{-5}$	9.65	1.07
	$1.50 \cdot 10^{-4}$	15.80	1.06
	$3.10 \cdot 10^{-4}$	30.85	0.99
10^{-2} *M* KH_2PO_4	$2.00 \cdot 10^{-5}$	1.50	0.75
$i_r = 5.50$ μA	$5.60 \cdot 10^{-5}$	4.10	0.73
	$9.00 \cdot 10^{-5}$	7.00	0.77
	$1.50 \cdot 10^{-4}$	11.90	0.78
	$3.10 \cdot 10^{-4}$	25.60	0.82

TABLE II (continued)

Electrolyte	*NaF concn. M*	i_d (μA)	i_d/C $\mu A/mM/l \cdot 10^{-2}$
	0.01 M HNO_3; pH 2.0		
KH_2PO_4 concn. = 0	$2.00 \cdot 10^{-5}$	3.20	1.60
$i_r = 0.55$ μA	$5.60 \cdot 10^{-5}$	8.70	1.55
	$9.00 \cdot 10^{-5}$	14.20	1.57
	$1.50 \cdot 10^{-4}$	22.90	1.53
	$3.10 \cdot 10^{-4}$	39.00	1.25
10^{-3} *M* KH_2PO_4	$2.00 \cdot 10^{-5}$	2.00	1.00
$i_r = 1.20$ μA	$5.60 \cdot 10^{-5}$	5.90	1.05
	$9.00 \cdot 10^{-5}$	9.30	1.05
	$1.5 \cdot 10^{-4}$	15.30	1.02
	$3.10 \cdot 10^{-4}$	30.00	0.96
10^{-2} *M* KH_2PO_4	$2.00 \cdot 10^{-5}$	1.28	0.64
$i_r = 5.10$ μA	$5.60 \cdot 10^{-5}$	3.90	0.65
	$9.00 \cdot 10^{-5}$	6.10	0.66
	$1.50 \cdot 10^{-4}$	10.90	0.72
	$3.10 \cdot 10^{-4}$	23.30	0.75
	Acetate buffer pH 3.60		
KH_2PO_4 concn. = 0	$2.00 \cdot 10^{-5}$	1.98	0.99
$i_r = 0.30$ μA	$5.60 \cdot 10^{-5}$	5.60	1.00
	$9.00 \cdot 10^{-5}$	8.75	0.97
	$1.50 \cdot 10^{-4}$	14.30	0.95
	$3.90 \cdot 10^{-4}$	33.00	0.84
10^{-4} *M* KH_2PO_4	$2.00 \cdot 10^{-5}$	1.75	0.87
$i_r = 0.30$ μA	$5.60 \cdot 10^{-5}$	4.70	0.84
	$9.00 \cdot 10^{-5}$	7.70	0.85
	$1.50 \cdot 10^{-4}$	12.80	0.85
	$2.00 \cdot 10^{-4}$	16.60	0.83
$2 \cdot 10^{-3}$ *M* KH_2PO_4	$2.00 \cdot 10^{-5}$	1.39	0.70
$i_r = 0.35$ μA	$5.60 \cdot 10^{-5}$	3.85	0.70
	$9.00 \cdot 10^{-5}$	6.25	0.70
	$1.50 \cdot 10^{-4}$	10.00	0.67
	$5.00 \cdot 10^{-4}$	34.90	0.69
0.01 *M* KH_2PO_4	$2.00 \cdot 10^{-5}$	1.18	0.59
$i_r = 0.50$ μA	$5.60 \cdot 10^{-5}$	3.00	0.53
	$9.00 \cdot 10^{-5}$	5.20	0.57
	$1.50 \cdot 10^{-4}$	9.00	0.60
	$2.00 \cdot 10^{-4}$	12.10	0.60
	Acetate buffer pH 4.0		
$1 \cdot 10^{-4}$ *M* KH_2PO_4	$2.00 \cdot 10^{-5}$	1.40	0.70
$i_r = 0.25$ μA	$5.00 \cdot 10^{-5}$	3.35	0.67
	$1.00 \cdot 10^{-4}$	6.70	0.67
	$1.50 \cdot 10^{-4}$	10.00	0.66
$2 \cdot 10^{-3}$ *M* KH_2PO_4	$5.60 \cdot 10^{-5}$	2.55	0.45
$i_r = 0.20$ μA	$1.10 \cdot 10^{-5}$	5.10	0.45
	$1.50 \cdot 10^{-4}$	7.90	0.52
	$3.20 \cdot 10^{-4}$	16.85	0.52

TABLE II (continued)

Electrolyte	*NaF concn. M*	i_a *(μA)*	i_a/C *μA/mM/l·10⁻²*
	Acetate buffer pH 4.0		
0.01 *M* KH_2PO_4 $i_r = 0.20$ μA	$2.00 \cdot 10^{-5}$	0.69	0.34
	$5.00 \cdot 10^{-5}$	1.85	0.37
	$1.00 \cdot 10^{-4}$	3.80	0.38
	$1.50 \cdot 10^{-4}$	5.80	0.39
	Acetate buffer pH 4.60		
$KH_2PO_4 = 0$ $i_r = 0.20$ μA	$2.00 \cdot 10^{-5}$	1.60	0.80
	$5.70 \cdot 10^{-5}$	4.50	0.80
	$9.20 \cdot 10^{-5}$	7.30	0.79
	$1.50 \cdot 10^{-4}$	12.20	0.81
	$3.10 \cdot 10^{-4}$	22.90	0.73
$2 \cdot 10^{-3}$ *M* KH_2PO_4 $i_r = 0.20$ μA	$2.00 \cdot 10^{-5}$	0.20	0.10
	$5.60 \cdot 10^{-5}$	0.79	0.14
	$1.20 \cdot 10^{-4}$	2.70	0.22
	$3.20 \cdot 10^{-4}$	7.65	0.23

Between pH 1 and 3.6 the relative effect of a given concentration of phosphate upon the sensitivity *k* is only slightly affected by pH. The effect is somewhat greater at pH 1 to 2 than at pH 3.6. For example, at pH 1 to 2 the sensitivity decreased about 1.6 times when a phosphate-free fluoride solution was made 0.001 *M* in phosphate and 1.4 times under the same circumstances at a pH of 3.6. In 0.001 *M* phosphate the ratios were 2. 3 and 1.75 respectively. From the analytical point of view it is important to note from Table II that the residual current at pH 1 to 2 increases much more by a given concentration of phosphate than at pH 3.6. In 0.01 *M* or more concentrated perchloric acid phosphate has an anodic depolarizing effect on the RAlE as is illustrated in Fig. 5. Apparently some highly dissociated or complex aluminum phosphate is being formed. It has been mentioned that in the absence of phosphate the residual current is smaller and better reproducible at pH 3.6 than at pH lower than 2. This, combined with the fact that the residual current increases considerably in the presence of phosphate at a pH lower than 2 while it is not affected by 0.001 *M* phosphate at

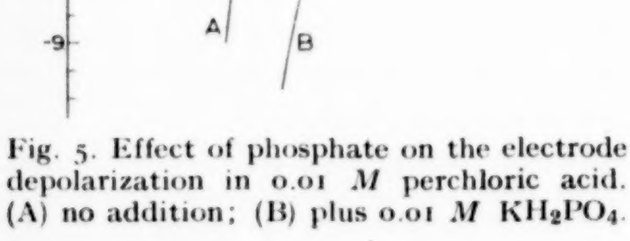

Fig. 5. Effect of phosphate on the electrode depolarization in 0.01 *M* perchloric acid. (A) no addition; (B) plus 0.01 *M* KH_2PO_4.

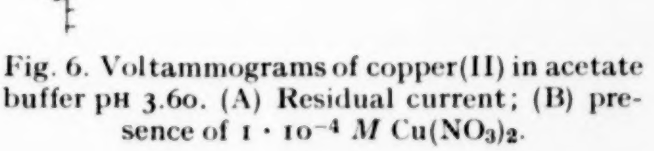

Fig. 6. Voltammograms of copper(II) in acetate buffer pH 3.60. (A) Residual current; (B) presence of $1 \cdot 10^{-4}$ *M* $Cu(NO_3)_2$.

pH 3.6, makes it evident that for the amperometric determination of fluoride a pH of about 3.5 is most suitable .With our electrode the residual current at pH 3.6 was found equal to 0.30-0.35 μA, even in the presence of 0.005 *M* phosphate. In the fluoride determination in a phosphate containing unknown the residual current can be determined in the supporting buffer, whereas at a pH less than 2 the residual current is unknown and could be estimated only if the phosphate concentration were known.

Effect of other substances

Experiments similar to those in Table II at different fluoride concentrations and in a buffer of pH 3.6 were repeated in the presence of 0.01 *M* alkali salts of nitrate, chloride and sulfate and 0.002 *M* calcium salts. No effect on the fluoride current was observed. Similarly, boric acid in a concentration of 0.01 *M* had no effect. On the other hand, ethylene diaminetetraacetic acid (EDTA) decreased the diffusion current, the effect being considerably greater at a pH 2 than in an acetate buffer of pH 3.6 (Table III). For example, the value of i_d/C at pH 2 decreased from $1.50 \cdot 10^2$ in the absence of EDTA to $0.80 \cdot 10^2$ in the presence of 0.001 *M* EDTA. At a pH of 3.6 the corresponding figures were $1.00 \cdot 10^2$ and $0.82 \cdot 10^2$. From the analytical view point it is significant that the value of i_d/C in the presence of EDTA remains constant over a wide range of fluoride concentrations. In 0.001 *M* EDTA at pH 3.6 it was necessary to wait after the first addition of fluoride for about 20 min before the fluoride current had attained its constant value. Upon additions of successive amounts of fluoride the final value of the current was attained within 5 min.

TABLE III

EFFECT OF EDTA ON THE FLUORIDE CURRENT AT —0.75 V *vs.* SCE

	NaF concentration	i_d (μA)	$i_d/C \cdot 10^{-2}$
	(1) *0.01 M nitric acid (pH 2.1) + 10^{-3} M EDTA*		
$i_r = 0.25$ μA	$2.00 \cdot 10^{-5}$	1.50	0.75
	$5.60 \cdot 10^{-5}$	4.50	0.80
	$9.00 \cdot 10^{-5}$	7.55	0.83
	$1.50 \cdot 10^{-4}$	12.30	0.82
	$2.00 \cdot 10^{-4}$	16.70	0.83
	(2) *Acetate buffer (pH 3.60) + 10^{-3} M EDTA*		
$i_r = 0.30$ μA	$2.00 \cdot 10^{-5}$	1.36	0.68[a]
	$5.60 \cdot 10^{-5}$	4.60	0.82
	$9.00 \cdot 10^{-5}$	7.45	0.82
	$1.50 \cdot 10^{-4}$	12.20	0.81
	$2.00 \cdot 10^{-4}$	16.75	0.83

[a] Current increases very slowly and reaches constancy after waiting 20 min.

Aluminum ions form stable complexes with fluoride at pH 3.6 and interfere seriously with the amperometric determination of fluoride. The effect of 10^{-4} *M* aluminum nitrate at a pH of 3.6 is illustrated in Table IV. As was to be expected, the i_d/C values increase with fluoride concentration. The aluminum can be made almost harmless by the addition of EDTA. Under these conditions the sensitivity of the electrode is about one half of that in the absence of aluminum and EDTA. The stability of aluminum fluoride complexes decreases with increasing hydrogen ion concentration. It is inter-

TABLE IV

EFFECT OF ALUMINUM IONS ON THE FLUORIDE CURRENT AT —0.75 V *vs.* SCE

	NaF concentration	i_d (μA)	$i_d/C \cdot 10^{-2}$
$0.1\ M\ HClO_4 + 10^{-4}\ M\ Al(NO_3)_3$			
$i_r = 1.40$ μA	$2.00 \cdot 10^{-5}$	3.50	1.75
	$5.60 \cdot 10^{-5}$	9.38	1.68
	$9.00 \cdot 10^{-5}$	14.69	1.63
	$1.20 \cdot 10^{-4}$	19.25	1.60
Acetate buffer (pH 3.60) + $10^{-4}\ M\ Al(NO_3)_3$			
$i_r = 0.25$ μA	$2.00 \cdot 10^{-5}$	0	0
	$5.00 \cdot 10^{-5}$	0.20	0.04
	$8.00 \cdot 10^{-5}$	0.60	0.07
	$1.00 \cdot 10^{-4}$	0.76	0.07
Acetate buffer (pH 3.60) + $10^{-4}\ M\ Al(NO_3)_3 + 10^{-3}\ M$ EDTA			
$i_r = 0.10$ μA	$5.60 \cdot 10^{-5}$	2.80	0.50
	$9.00 \cdot 10^{-5}$	4.55	0.50
	$1.10 \cdot 10^{-4}$	6.61	0.59
	$1.50 \cdot 10^{-4}$	8.79	0.59

TABLE V

EFFECT OF IRON(III) AND IRON(II) AT —0.75 V

	NaF concentration	i_d (μA)	$i_d/C \cdot 10^{-2}$
0.01 M nitric acid (pH 2.1); absence of iron; $i_d/C = 1.6 \cdot 10^2$ with $10^{-3}\ M\ Fe(NO_3)_3$			
$i_r = 0.45$ μA	$2.00 \cdot 10^{-5}$	0.20	0.10
	$5.60 \cdot 10^{-5}$	0.65	0.11
	$9.10 \cdot 10^{-5}$	0.90	0.10
	$1.50 \cdot 10^{-4}$	2.10	0.14
Acetate buffer (pH 3.60); absence of iron: $i_d/C = 0.98 \cdot 10^2$ with $10^{-3}\ M\ Fe(NO_3)_3$			
$i_r = 0.25$ μA	$2.00 \cdot 10^{-5}$	1.00	0.50
	$5.60 \cdot 10^{-5}$	3.70	0.65
	$9.00 \cdot 10^{-5}$	6.35	0.70
	$1.50 \cdot 10^{-4}$	10.90	0.72
with $10^{-3}\ M\ Fe(NO_3)_3 + 0.01\ M\ NH_2OH \cdot HCl$			
$i_r = 0.35$ μA	$2.00 \cdot 10^{-5}$	2.35	1.10
	$5.60 \cdot 10^{-5}$	6.10	1.07
	$9.10 \cdot 10^{-5}$	9.90	1.07
	$1.50 \cdot 10^{-4}$	15.40	1.02

esting to note in Table IV that aluminum in a concentration of 10^{-4} *M* does not have an effect at all on the fluoride current in 0.1 *N* perchloric acid, even though the depolarization of the electrode at this pH is attributed to formation of aluminum fluoride complexes. This anomalous behavior may be related to the permeability for fluoride ions and hydrofluoric acid of a film on the electrode whereas the film is impermeable to hydrogen ions.

Contrary to the behavior of aluminum ions it was found that ferric iron even in a concentration as high as 0.001 *M* has relatively little effect on the fluoride current at pH 3.6. It is seen in Table V that the sensitivity of the electrode for fluoride drops is relatively little under these conditions. The ferric iron can be made entirely harmless by reducing agents like hydroxylamine hydrochloride (Table V). The interference by 0.001 *M* ferric iron at pH 2 is very great as is illustrated in Table V. In an acetate buffer of pH 3.6 the ferric iron apparently is almost completely hydrolyzed or present in the form of fairly stable acetate complexes. On the other hand, at a pH of 2 it is mainly present in the form of ferric iron which forms stable complexes with fluoride.

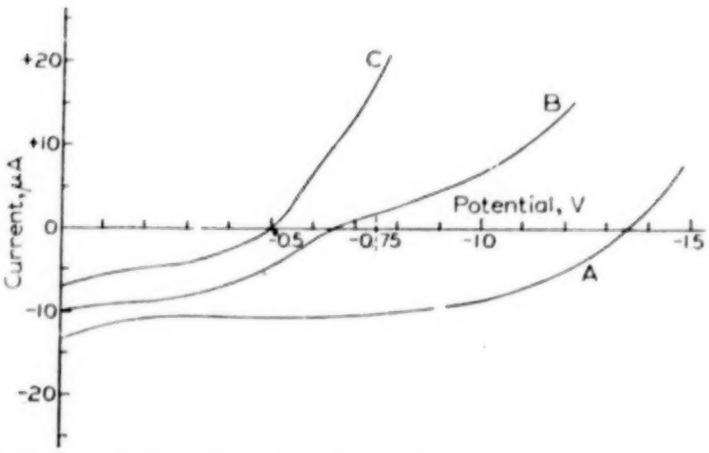

Fig. 7. Effect of copper(II) on voltammogram of fluoride (oxygen-free) at pH 3.6. (A) $1 \cdot 10^{-4}$ *M* fluoride; (B) as (A) with 10^{-4} *M* copper (II); (C) as (A) with $5 \cdot 10^{-4}$ *M* copper (II).

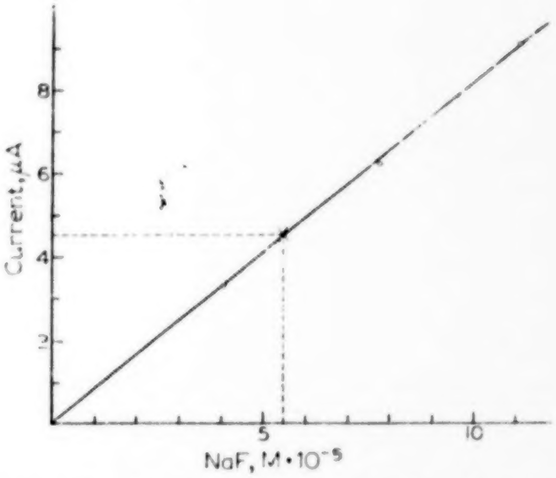

Fig. 8. Determination of fluoride in Minneapolis water by the standard addition technique. X presents the current of the unknown (corrected for residual current); fluoride content: 1.04 p.p.m.

As can be seen from Fig. 6, copper(II) cathodically depolarizes the aluminum electrode and yields a drawn-out irreversible reduction wave with the formation of metallic copper. Since the amperometric determination of fluoride is carried out at —0.75 V (*vs.* SCE), copper(II) interferes seriously because these ions yield a considerable reduction current at this potential. The situation is made clear in Fig. 7. The interference of copper can be eliminated to a large extent by making the solution 0.001 *M* in EDTA. But even then, a slight reduction current of copper is observed at —0.75 V. Although the fluoride current at this potential was found to be proportional to concentration in the presence of copper(II) and EDTA, the difficulty remains to find out the proper correction in the residual currents of unknowns for the presence of copper(II).

Quite generally, oxidizing substances like oxygen, silver ions, ceric cerium etc. all interfere for the same reason as copper(II) does. They must be removed from solution prior to the amperometric determination of fluoride. This is actually a simple matter and it can be accomplished by classical methods.

AMPEROMETRIC DETERMINATION OF FLUORIDE

Application to fluoride analysis in water

In order to be independent of the reproducibility of the electrode, the method of "standard addition"[6] is recommended; it has been used by us in all our fluoride determinations. No effort has been made to develop a technique using semimicro or micro volumes of fluoride. In general, we used 50 ml of the sample in the electrolysis cell. The recommended procedure has been tested with various samples of potable water.

PROCEDURE

Residual current. For the determination of the residual current transfer 50 ml of distilled water into the electrolysis cell, add 1 ml of 1 *M* sodium acetate and 0.5 ml of glacial acetic acid, place the RAlE in position, rotate at 600 r.p.m. and measure the residual current at —0.75 V *vs.* SCE.

Unknown. Place a suitable volume of the sample into a 50-ml volumetric flask and adjust to pH 3.6 by addition of 1 ml of 1 *M* sodium acetate and 0.5 ml of glacial acetic acid, then dilute to 50 ml. Transfer the solution to the electrolysis cell and remove oxygen by bubbling nitrogen for at least 5 min. While nitrogen is passed through, introduce the RAlE and start its rotation at 600 r.p.m. Care must be taken to avoid formation of gas bubbles at the electrode which tend to disturb the diffusion layer and cause irregular readings. Apply a potential of —0.75 V and record the current after it has attained a constant value (usually less than 10 min). Add known amounts of fluoride from a microburet, continue passage of nitrogen and record the steady current after each increment addition. Plot the increase in current after each successive addition of fluoride *vs.* the concentration of added fluoride (consider volume correction) and construct a straight line as illustrated in Fig. 8. Correct the current measured in the unknown for the residual current and read the fluoride concentration from the graph.

Example

Minneapolis city water was analysed by the above procedure. The residual current was 0.3 μA (anodic). Sodium acetate and acetic acid were added to the undiluted sample. The fluoride current measured was 4.8 μA. After correction for the residual current, a value of 4.5 μA is found. According to the plot in Fig. 8 this current corresponds to a fluoride concentration of $5.5 \cdot 10^{-5}$ *M* or 1.04 p.p.m. is found.

Notes

1. The linear relation between current and fluoride concentration holds up to a concentration of about $3 \cdot 10^{-4}$ *M* or about 6 p.p.m. of fluoride. The original sample need not to be diluted when the fluoride concentration is less than about 2 p.p.m.

2. The precision obtained by running 5 separate experiments with Minneapolis city water was 3%. The precision and accuracy decrease with decreasing fluoride content. However, concentrations of 0.2 p.p.m. fluoride still could be estimated with an accuracy and precision of 10%. At such low concentrations of fluoride the error is caused mainly by the uncertainty in the residual current of the unknown.

3. Moderate amounts of phosphate and sulfate do not interfere. Thus the method has great advantages over colorimetric or spectrophotometric methods which require distillation.

4. When the order of magnitude of the fluoride concentration in the sample is not known it can be estimated by measuring the current at —0.75 V *vs.* SCE (absence of oxygen). From the known sensitivity of the electrode the fluoride content is readily estimated with fair accuracy.
5. The RAIE could be installed in water works in which water is being fluorinated so that constancy of the fluoride content of the water could be tested.

Results of analyses

Some 20 samples of known fluoride content (but unknown to the analyst) were prepared in which the fluoride concentration varied between 0.2 and 2 p.p.m. Some samples contained 0.001 *M* phosphate, others 0.005 *M* sulfate or 0.01 *M* chloride or combinations. The fluoride content found checked within 10% (and usually better) with the known content.

One sample of potable water was analyzed for fluoride in order to test the reliability of the method. Minneapolis city water: found 1.06 ± 0.02 p.p.m. (average of 5 determinations). The same sample was analyzed by Dr. L. SINGER of the Department of Physiological Chemistry of the University of Minnesota, using the method of MEGREGIAN[8] which involves distillation, with the following results: 1.04; 1.09; 1.11; 1.13; 1.18; 1.28. If the last value is omitted, the average is 1.11 p.p.m.

Eight samples of raw, non-potable natural waters were obtained from the Minneapolis Health Department. These samples from different parts of the State of Minnesota were of widely different composition and had been analyzed by the Health Department using a slight modification of the procedure of MEGREGIAN[8]. Some of the samples, contained considerable amounts of solids. The results of our method are compared in Table VI with those reported by the Department of Health. The agreement is gratifying.

TABLE VI

FLUORIDE ANALYSIS OF WATER SAMPLES FROM THE MINNESOTA HEALTH DEPARTMENT

Sample number	*Fluoride in p.p.m.*	
	RAIE[a]	*Colorimetric method*
8284	0.25 0.28	0.30 (without distillation)
8712[b]	0.40 0.43	0.25 (without distillation)
8136	1.06 1.10	1.10 (without distillation)
8285	1.35 1.35	1.20 (without distillation)
8408	1.10 1.19	1.10 (without distillation)
8380[b]	0.28 0.30	0.40 (after distillation)
8625[b]	0.20 0.25	0.42 (without distillation) 0.32 (after distillation)
8286	0.22 0.26	0.20 (without distillation)

[a] Results of two independent analyses.

[b] Samples contained large quantities of solid.

ACKNOWLEDGEMENTS

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SUMMARY

A simple and rapid amperometric method is described for the determination of traces of fluoride by measuring the anodic current at the RAlE at —0.75 V *vs.* SCE. In order to be independent of varying sensitivity of the RAlE, use is made of the standard addition technique.

Proportionality between current and concentration is found between 0.2 and 6 p.p.m. of fluoride. Chloride, sulfate, nitrate, alkali and earth alkali ions do not interfere. Phosphate decreases the sensitivity but does not interfere. Aluminum ions interfere but can be made harmless by EDTA. Oxidizing agents (including oxygen) must be removed. The method gives excellent results in potable and natural waters.

RÉSUMÉ

Une méthode ampérométrique simple et rapide est proposée pour le dosage de traces de fluorure, en mesurant le courant anodique à l'électrode tournante d'aluminium à —0.75 V (*vs.* ECS). Ce procédé peut être appliqué à l'analyse de l'eau.

ZUSAMMENFASSUNG

Es wird eine einfache und schnelle ampèrometrische Methode beschrieben zur Bestimmung von Spuren von Fluorid durch Messung des anodischen Stromes einer drehenden Aluminium Elektrode bei —0.75 V gegen ECS. Diese Methode kann bei der Wasseranalyse verwendet werden.

REFERENCES

[1] I. M. KOLTHOFF AND C. J. SAMBUCETTI, *Anal. Chim. Acta*, 21 (1959) 17.
[2] I. M. KOLTHOFF AND C. J. SAMBUCETTI, *Anal. Chim. Acta*, 21 (1959) 155.
[3] N. BAKER AND J. MORRISON, *Anal. Chem.*, 27 (1955) 1307.
[4] S. MEGREGIAN, *Anal. Chem.*, 29 (1957) 1063.
[5] J. K. JOHANNESSON, *Chem. & Ind. (London)*, (1957) 480.
[6] I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Vol I, Interscience Publishers, Inc., New York 1952, p. 377.
[7] W. F. HILLEBRAND AND G. H. LUNDELL, *Applied Inorganic Analysis*, John Wiley and Sons, Inc., New York 1953, p. 744.
[8] S. MEGREGIAN, *Anal. Chem.*, 26 (1954) 1161.

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DIRECT ESTIMATION OF NIOBIUM BY N-BENZOYL-N-PHENYLHYDROXYLAMINE

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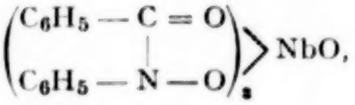
The preparation of various complexes of niobium and tantalum with a number of organic reagents has been attempted[1,2]. None of the experiments, however, have resulted in the formation of a compound of definite composition, suitable for analytical work. SÜE[3], on the other hand, claims to have isolated an oxine complex of niobium which apparently corresponds to the composition $Nb_2O_5 \cdot 5.5\ C_9H_7ON \cdot 4\ H_2O$.

In a previous paper[4], N-benzoyl-N-phenylhydroxylamine was shown to be an effective reagent not only for the separation of niobium and tantalum from each other by the control of pH but also for the separation of the former element from other interfering ions by the proper control of conditions in the presence of sequestering agents. In that work, the precipitates of niobium and tantalum were ignited to their respective oxides before their final weighing.

Further study reveals that the buff-coloured precipitate of niobium, obtained after digestion on the boiling water bath at a pH lower than 6.5, is insoluble in water, ethyl and amyl acetates, acetone, carbon tetrachloride and benzene, but highly soluble in chloroform. Niobium's excellent solubility in chloroform classifies it as a member of the internal complex salts, whose molecules contain no free acid and basic groups.

The complex dried at 110° indicates the composition to be



$$\left(\begin{array}{l} C_6H_5 - C = O \\ \qquad\quad | \\ C_6H_5 - N - O \end{array}\right)_2 \!\!> NbO,$$

where the percentage of niobium is only 12.46%. This complex, even when air-dried, is stable up to a temperature of about 229° which implies its formation by the elimination of water, during the reaction of the niobic acid with the reagent on the boiling water bath.

Owing to its stability to heat and insolubility in hot water, the niobium complex, after being filtered, washed and dried, can be directly weighed for its gravimetric estimation.

The tantalum precipitate, however, is of indefinite composition and loses weight with the rise of temperature. Both the niobium and tantalum precipitates are converted to their oxides at about 500°.

EXPERIMENTAL

All the chemicals and standard solutions used were the same as previously reported[4].

Composition

The niobium complex after precipitation, according to the procedure described earlier[4], was washed with hot water and dried at 110°. A portion of the complex was ignited to oxide to determine the percentage of niobium present, and from the other portion, the nitrogen content of the complex was estimated by the Kjeldahl method.

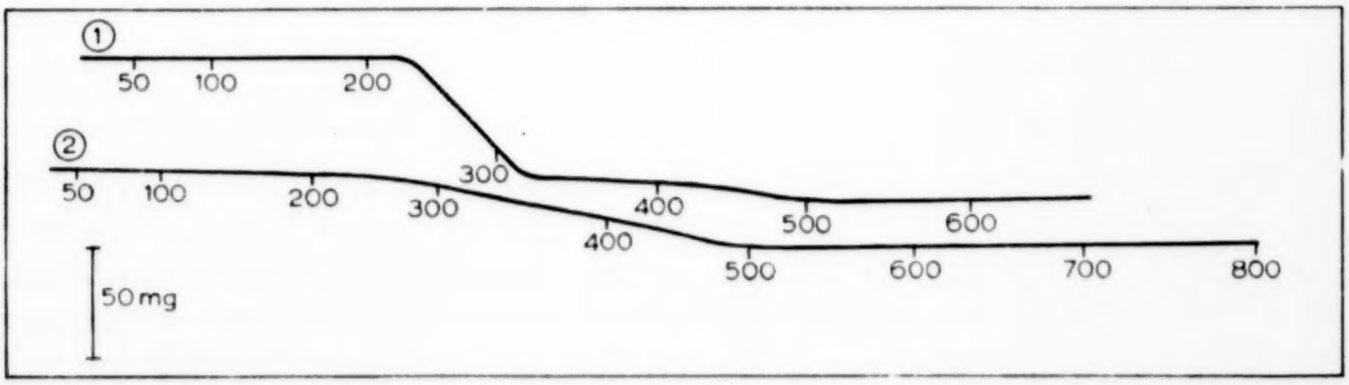


Fig. 1. Thermolysis curves: (1) Niobium complex. (2) Tantalum complex.

Thus the composition was found to be $NbO(C_{13}H_{10}NO_2)_3$ [% Nb calc. 12.46, % N_2 calc. 5.64; % Nb found 12.42, 12.44, % N_2 found 5.58, 5.62].

The thermolysis curves (Fig. 1) show that the niobium complex, dried at 110°, is stable up to about 229°, but that the tantalum complex loses weight with the increase of temperature; both complexes are completely changed to their oxides at about 500°.

Procedure

The niobium, after precipitation by the reagent solution, as described in the previous paper[4], was digested on the boiling water bath for about an hour and was then filtered through a weighed, sintered Gooch crucible, washed thoroughly with hot water, dried at 110° and weighed. The weight of complex multiplied by the factor 0.1783 gave the weight of Nb_2O_5. Tantalum, when present, was estimated from the filtrate of niobium. The tantalum precipitate, however, was ignited to oxide before weighing. The results are given in Table I.

For the separation of niobium from other ions in the presence of EDTA, a procedure similar to that discussed previously[4] was followed.

TABLE I

Nb_2O_5 taken mg	*Ta_2O_5 taken mg*	*Wt. of Nb-complex mg*	*Nb_2O_5 found mg*	*Ta_2O_5 found mg*
9.6	—	53·2	9·5	—
24.0	—	135·7	24.2	—
48.0	8.6	(i) 271.0	(i) 48.3	(i) 8.2
		(ii) 270.3	(ii) 48.1	(ii) 8.2
9.6	43·0	(i) 55·2	(i) 9.8	(i) 42.7
		(ii) 55·5	(ii) 9.8	(ii) 42.6

SUMMARY

N-benzoyl-N-phenyl hydroxylamine, with niobium, forms a complex of composition $NbO(C_{13}H_{10}NO_2)_3$ which is stable up to a temperature of 229°. Niobium, thus, can be separated from tantalum and other elements as this complex and weighed directly after being dried at 110°.

RÉSUMÉ

La N-benzoyl-N-phénylhydroxylamine est proposée comme réactif pour le dosage gravimétrique du niobium. On peut ainsi séparer le niobium d'avec d'autres éléments, en particulier d'avec le tantale.

ZUSAMMENFASSUNG

N-Benzoyl-N-phenylhydroxylamin eignet sich als Fällungsreagenz zur gravimetrischen Bestimmung von Niob, das sich damit von Tantal und anderen Elementen trennen lässt.

REFERENCES

[1] A. Rosenheim and E. Roehrich, *Z. anorg. Chem.*, 209 (1932) 342.
[2] H. Funk and W. Baumann, *Z. anorg. Chem.*, 231 (1937) 264.
[3] P. Süe, *Compt. rend.*, 196 (1933) 1022.
[4] A. K. Majumdar and A. K. Mukherjee, *Anal. Chim. Acta*, 19 (1958) 23.

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PHOTOMETRIC DETERMINATION OF QUATERNARY AMMONIUM COMPOUNDS WITH HEXANITRODIPHENYLAMINE. I.

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Many recent methods for the determination of amines and quaternary ammonium compounds are based on the use of reagents which yield compounds extractable from aqueous solutions with chloroform or similar solvents. The majority of the published methods employ acid–base indicators of the sulphophthalein type. The extracted compounds have high molar extinctions and can be directly determined photometrically. For the determination of quaternary ammonium compounds bromothymol blue[1], bromocresol purple[2,3], and bromophenol blue[4-6] have been used. The literature has been summarized by BALLARD *et al.*[7]. Similar methods have been used for the determination of amines[8,9].

The indicator methods appear in general to be strongly dependent on the experimental conditions and are only applicable for the determination of certain kinds of quaternary ammonium compounds.

A few other extraction methods have also been used. High molecular quaternary ammonium compounds yield iodides, which are extractable with chloroform; the extracted iodide can be determined photometrically after oxidation to free iodine[10]. Atropine can be determined by extracting atropine picrate with chloroform; the picrate is reduced to picramic acid and determined photometrically[11].

We have found that hexanitrodiphenylamine with quaternary ammonium compounds yields compounds which can be extracted from aqueous solution with organic solvents such as chloroform or methylene chloride. The compounds have high molecular extinctions and therefore very small amounts of quaternary ammonium compounds can be determined by direct photometric measurements.

In the present paper investigations of the reagent and of the general experimental conditions for the determination of quaternary ammonium compounds are described.

Little information is available concerning the physico-chemical properties of hexanitrodiphenylamine (dipicrylamine). SCHROEDER *et al.*[21] reported the spectra in acid and basic ethanol solution as well as the molar extinction at the maxima. KERTES AND GOLDSCHMIDT[12] determined the corresponding spectra in dioxane–water solution. On the basis of potentiometric measurements they found the apparent $pK_a = 0.35$ (dioxane). TREADWELL AND HEPENSTRICK[13] found $pK_a = 8.15$ (water).

Hexanitrodiphenylamine yields slightly soluble compounds with organic bases and has been used as a precipitant for alkaloids and other bases[14,15]. ACKERMAN AND MAUER[16] found that quaternary ammonium compounds gave precipitates which were soluble in acetone, thus permitting their photometric determination. SAMUELS-

SON[17] determined choline and choline esters according to this principle and SIMON-DORLET[18] determined divalent quaternary ammonium compounds. The compounds formed contained hexanitrodiphenylamine in the form of univalent anions.

KERTES[19,20] has studied reactions between hexanitrodiphenylamine and organic bases in dioxane solution and has also given a method for the determination of pyridine.

EXPERIMENTAL

Purification of the reagent

A saturated chloroform solution of dipicrylamine (pro analysi, Merck) was applied to a chromatographic column containing kieselguhr (Hyflo Super Cel) as the supporting phase, phosphate buffer (pH = 7) as the stationary phase and chloroform as the mobile phase. The column was eluted with chloroform, and the eluate was collected in 5-ml portions. The concentration of solute in the eluate was determined by measurement of the extinction at 380 mμ. Results are shown in Fig. 1.

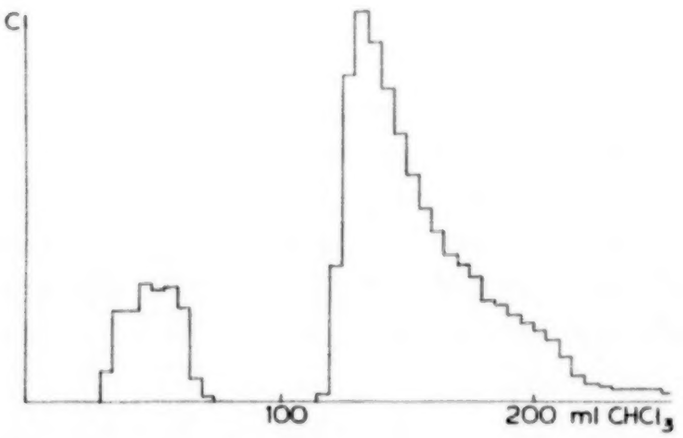

Fig. 1. Chromatogram of dipicrylamine (analytical grade) containing hexa- and pentanitrodiphenylamine.

The eluate fractions were evaporated and the residues were dissolved in ethanol. The absorption spectra of the ethanolic solutions were determined after addition of acid (0.05 ml of 5 *N* HCl per 100 ml) and base (0.05 ml of 5 *N* NaOH per 100 ml). The fractions 30–75 ml were found to yield identical spectra; comparison with SCHROEDER *et al.*[21] indicated that they contained 2,2′,4,4′,6-pentanitrodiphenylamine. The fractions after 115 ml were found to contain 2,2′,4,4′,6,6′-hexanitrodiphenylamine by similar methods.

Determination of dissociation constants

The dissociation constants of the pure substances obtained by the foregoing procedure were determined according to SAGER *et al.*[22]. The photometric determinations were carried out with a Uvispek spectrophotometer using a band width of 5 Å at a temperature of 20° ± 1°. The pH determinations were performed at the same temperature with a glass electrode calibrated against potassium biphthalate 0.05 *M*. The readings are believed to be correct within ± 0.01 pH unit.

All determinations were carried out in phosphate buffers with an ionic strength of about $6 \cdot 10^{-3}$ using the same concentration of substances (2 mg per 1000 ml). The only exception was the determination at pH 0.22, which was done in hydrochloric acid. In order to obtain sufficiently high extinction a layer thickness of 4 cm was employed. The buffer solutions were used as blanks. The phosphate has no absorption in the wavelength region used for the calculations, and as the isosbestic point is well-defined there is probably no other disturbing effect from the buffer system.

The constants determined were the apparent dissociation constants which are defined:

$$\frac{a_{H_3O^+} \cdot c_b}{c_a} = K_a$$

where $a_{H_3O^+}$ = hydronium ion activity, c_b = concentration of base, and c_a = concentration of acid.

At constant concentration of nitro compound the following expression for pK_a is obtained:

$$pK_a = \text{pH} - \log \frac{E - E_a}{E_b - E}$$

where E = extinction found, E_a = extinction with the compound in acid form, and E_b = extinction with the compound in basic form.

The calculations were carried out using extinction values at wavelengths where the extinction of the base had a rather flat maximum while the extinction of the acid was very low. The results for hexanitrodiphenylamine appear in Fig. 2 and Table I and for pentanitrodiphenylamine in Fig. 3 and Table II.

TABLE I

PHOTOMETRIC DETERMINATION OF APPARENT DISSOCIATION CONSTANT OF HEXANITRODIPHENYLAMINE

pH	E^{430}	pK_a
0.22	0.038	—
2.60	0.252	2.80
2.74	0.297	2.80
2.80	0.311	2.81
3.07	0.393	2.82
6.96	0.591	—

Determination of partition coefficients

10.00 ml of approximately $4 \cdot 10^{-5}$ *M* solutions of the nitro compounds in the organic solvent (chloroform, methylene chloride or ethylene chloride) were shaken to equilibrium with 10.00 ml of the aqueous phase. The concentration of the nitro compound was determined spectrophotometrically in the organic phase. The pH of the aqueous phase was determined after the shaking was completed. The temperature and error in the pH determinations were the same as in the determination of the dissociation constants. The spectrophotometric determinations were carried out with a Beckman spectrophotometer model B.

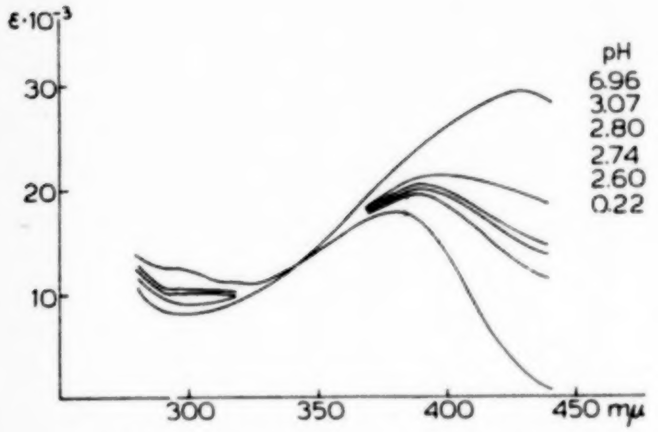

Fig. 2. Absorption spectra of hexanitrodiphenylamine in water of varying acidity.

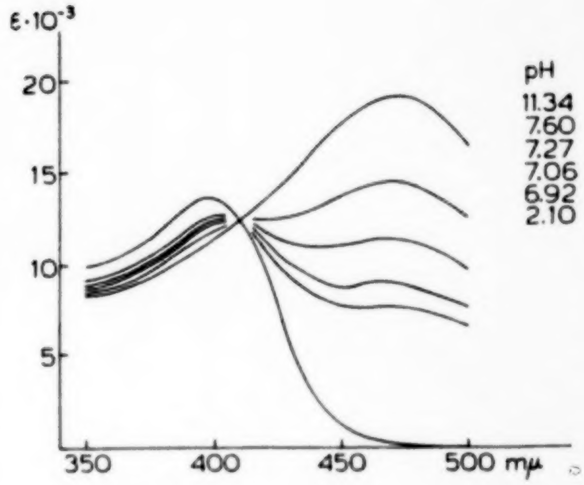

Fig. 3. Absorption spectra of pentanitrodiphenylamine in water of varying acidity.

TABLE II

PHOTOMETRIC DETERMINATION OF APPARENT DISSOCIATION CONSTANT OF PENTANITRODIPHENYLAMINE

pH	E^{470}	pK_a
2.10	0.005	—
6.92	0.138	7·11
7.06	0.161	7·13
7·27	0.204	7·12
7.60	0.261	7·11
11.34	0·343	—

TABLE III

PARTITION COEFFICIENTS

System	K_d	
	Hexanitrodiphenylamine	*Pentanitrodiphenylamine*
$CHCl_3/H_2O$	$6.5 \cdot 10^3$	$3.2 \cdot 10^3$
CH_2Cl_2/H_2O	$4.9 \cdot 10^4$	$2.0 \cdot 10^3$
$CH_2Cl.CH_2Cl/H_2O$	$5.5 \cdot 10^4$	—

The chloroform used was of pharmaceutical grade. The methylene chloride and ethylene chloride were purified by shaking with sodium carbonate solution and water and by distillation after drying. As aqueous phases 0.05 M phosphate buffers were employed.

The partition coefficients are defined as:

$$\frac{c_{a(\mathrm{org})}}{c_{a(\mathrm{H_2O})}} = K_d$$

In the organic phase the nitro compounds occur only as acids; in the aqueous phase they are protolyzed to a varying degree. Since the organic and aqueous phases are of equal volume the following equations are obtained:

$$c_{a(\mathrm{org})} = E.K$$

$$c_{a(\mathrm{H_2O})} + c_{b(\mathrm{H_2O})} = (E_{\mathrm{tot}} - E)\,.\,K$$

$$K_d = \frac{E}{E_{\mathrm{tot}} - E}\left(1 + \frac{K_a}{a_{\mathrm{H_3O^+}}}\right)$$

where E = extinction of the organic phase after shaking, and E_{tot} = extinction of the organic phase before shaking. The results are given Table III.

Spectra in chloroform and methylene chloride solutions

The absorption spectra of the nitro compounds were determined after addition of acid (1 mg of trichloroacetic acid per 10 ml) and of base (1 mg of piperidine per 10 ml). Spectra were also determined for the complex formed between the nitro compounds and a quaternary ammonium compound (tetraethylammonium bromide).

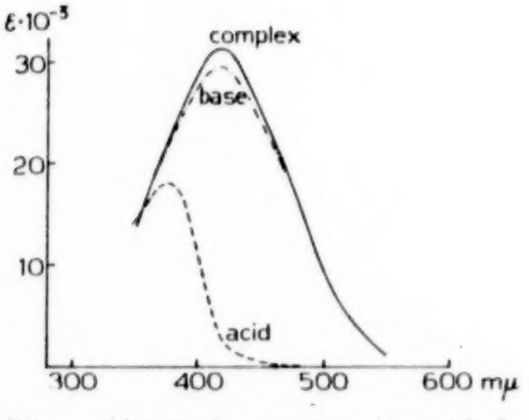

Fig. 4. Absorption spectra in methylene chloride of hexanitrodiphenylamine after addition of acid (trichloroacetic acid) and base (piperidine) and of its complex with tetraethylammonium ion.

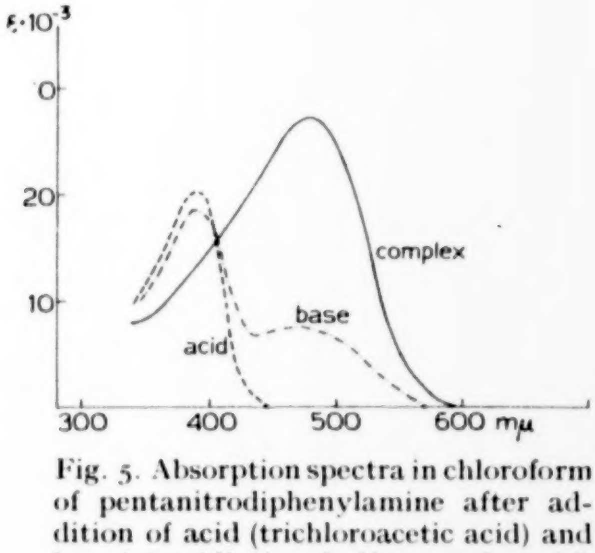

Fig. 5. Absorption spectra in chloroform of pentanitrodiphenylamine after addition of acid (trichloroacetic acid) and base (piperidine) and of its complex with tetraethylammonium ion.

The solution of this complex was obtained by extraction with methylene chloride or chloroform from an aqueous solution at pH 11 for hexanitrodiphenylamine and at pH 13–14 for pentanitrodiphenylamine. The results are shown in Fig. 4 (hexanitrodiphenylamine) and Fig. 5 (pentanitrodiphenylamine). There are only small differences between the spectra in chloroform and in methylene chloride.

DISCUSSION

The chromatographic investigation showed that commercially available hexanitrodiphenylamine (dipicrylamine p.a. Merck) is contaminated with pentanitrodiphenylamine. Only experiments at pH 7 are described above, but corresponding experiments at pH 8, 9, 10 and 11 showed no further components. At the higher pH values the elution of the hexanitro compound takes place very slowly.

The great difference in elution rate is caused primarily by the difference in the pK_a values (Tables I and II). The value found for hexanitrodiphenylamine diverges very remarkably from that reported in the literature[13]. However, this is probably due to the fact that the latter value was determined as the half-titre point in the titration of the sodium salt of the compound with hydrochloric acid. Since hexanitrodiphenylamine is very slightly soluble, precipitation occurs during the titration.

The remarkably strong acidic properties of hexanitrodiphenylamine as well as the difference in strength between the hexa- and pentanitro compounds are, of course, connected with the positively polarized nitro groups of the molecules (*cf.* 4-nitrophenol: $pK_a = 7.2$, 2,4-dinitrophenol: $pK_a = 4.0$ and 2,4,6,-trinitrophenol: $pK_a = 0.8$).

The partition coefficients for the hexa- and pentanitro compounds differ only slightly (Table III), but because of the great difference in the dissociation constants, the compounds are very easily separated (Fig. 6). The values shown in the figure have been calculated from the pK_a and K_a values obtained for the two nitro compounds.

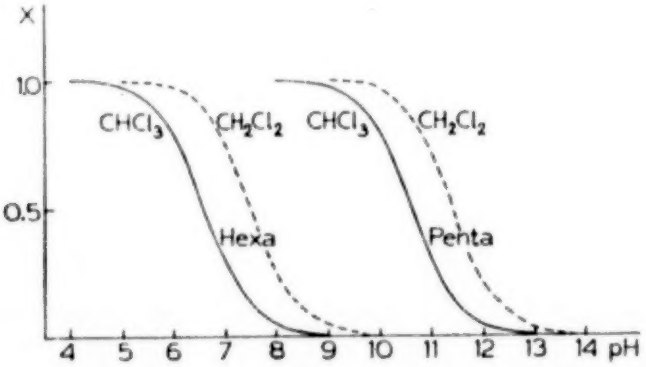

Fig. 6. Distribution of hexa- and pentanitrodiphenylamine between aqueous and organic phases (chloroform or methylene chloride) at different pH values. (X = part of total amount in the organic phase. Both phases have equal volumes)

The difference in the absorption spectra of the complexes formed from the hexa- and pentanitro compounds and a compound containing tetraethylammonium ion is striking. Hexanitrodiphenylamine yields a complex with the extinction maximum at 420 mμ and the molar extinction at the maximum is $3.1 \cdot 10^4$ (Fig. 4). The complex containing the pentanitro compound has its extinction maximum at 480 mμ and the molar extinction at the maximum is $2.7 \cdot 10^4$. At 420 mμ this complex has the molar extinction $1.7 \cdot 10^4$ (Fig. 5).

From Fig. 4 it can be seen that free acid (hexanitrodiphenylamine) has a significant extinction at the extinction maximum of the complex (420 mμ). It is therefore necessary to extract the complex at such a pH that practically no free acid is extracted.

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The pH should exceed 10 when chloroform is used and 11 when methylene chloride is used.

The necessity of employing a reagent which is free from pentanitrodiphenylamine is also clear from Figs. 4, 5 and 6. At a pH of less than 12 more or less of the pentanitrodiphenylamine is extracted with chloroform (with methylene chloride at pH below 13) and this contaminates the complex of hexanitrodiphenylamine extracted at the same time. Pentanitrodiphenylamine interferes in the spectrophotometric determination because it has a relatively high extinction at the extinction maximum for the complex (420 mμ).

SUMMARY

Dissociation contants, partition coefficients and absorption spectra have been determined for hexanitrodiphenylamine and pentanitrodiphenylamine. The two compounds have quite different dissociation constants and can be easily separated. Both substances give compounds with quaternary ammonium ions which can be extracted with chloroform or methylene chloride from an aqueous solution. To obtain a pure hexanitrodiphenylamine compound the reagent must be free from pentanitrodiphenylamine and the extraction made at high pH.

RÉSUMÉ

Des déterminations de constantes de dissociation, de coefficients de partage et de spectres d'absorption ont été effectuées pour l'hexanitrodiphénylamine et la pentanitrodiphénylamine. Ces deux substances donnent avec les ions ammonium quaternaires des composés que l'on peut extraire dans le chloroforme ou le chlorure de méthylène.

ZUSAMMENFASSUNG

Es wurden die Dissoziationskonstanten, Verteilungskoeffizienten und Absorptionsspektren von Hexanitrodiphenylamin und Pentanitrodiphenylamin bestimmt. Diese beiden Substanzen bilden mit quaternären Ammonium Ionen Verbindungen, die sich mit Chloroform oder Methylenchlorid aus einer wässrigen Lösung extrahieren lassen.

REFERENCES

1 K. R. Gottlieb, *Dansk Tidsskr. Farm.*, 27 (1953) 199.
2 P. L. Perlman, C. B. Johnsson and R. E. Kosinki, *J. Am. Pharm. Assoc., Sci. Ed.*, 42 (1953) 483.
3 J. Fogh, P. O. H. Rasmussen and K. Skadhauge, *Anal. Chem.*, 26 (1954) 392.
4 M. E. Auerbach, *Ind. Eng. Chem., Anal. Ed.*, 15 (1943) 492.
5 M. E. Auerbach, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 739.
6 E. L. Colichman, *Anal. Chem.*, 19 (1947) 430.
7 C. W. Ballard, J. Isaacs and P. G. W. Scott, *J. Pharm. and Pharmacol.*, 6 (1954) 971.
8 B. B. Brodie and S. Ulenfriend, *J. Biol. Chem.*, 158 (1945) 705.
9 A. O. Gettler and I. Sunshine, *Anal. Chem.*, 23 (1951) 779.
10 R. Reiss, *Arzneimittel-Forsch.*, 6 (1956) 77.
11 A. A. Semenycheva, *Aptechnoe Delo*, 2 (1953) 18.
12 S. Kertes and J. M. E. Goldschmidt, *J. Chem. Soc.*, (1956) 401.
13 W. D. Treadwell and H. Hepenstrick, *Helv. Chim. Acta*, 32 (1949) 1903.
14 Langhans, *Nitrocellulose*, 9 (1938) 19.
15 Langhans, *Nitrocellulose*, 10 (1939) 103, 130.
16 D. Ackerman and H. Mauer, *Z. physiol. Chem.*, 279 (1943) 114.
17 G. Samuelsson, *J. Pharm. and Pharmacol.*, 5 (1953) 239.
18 Simon-Dorlet, *J. pharm. Belg.*, 9 (1954) 106.
19 S. Kertes, *Anal. Chim. Acta*, 15 (1956) 73.
20 S. Kertes and V. Kertes, *Anal. Chim. Acta*, 15 (1956) 154.
21 W. A. Schroeder, P. E. Wilcox, K. N. Trueblood and A. O. Dekker, *Anal. Chem.*, 23 (1951) 1740.
22 E. E. Sager, M. R. Schovley and S. F. Acree, *J. Research Natl. Bur. Standards*, 35 (1945) 521.

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THE POLAROGRAPHY OF LEAD STYPHNATE*

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INTRODUCTION

In the course of a recent study of styphnate materials it became necessary to determine the lead-styphnate ratio existing in the same solution. This was required to provide information regarding the presence of free styphnic acid, or other styphnates in lead styphnate solutions. Since both lead and styphnic acid are reducible at the dropping mercury electrode it appeared that the determination of these two species might conveniently be made by polarography. This paper describes the work carried out to develop a method for this determination.

EXPERIMENTAL AND DISCUSSION

All polarography described in this paper was carried out on a Cambridge Pen Recording Polarograph and *versus* the mercury pool anode. A Cambridge Univector Unit[1] was used in conjunction with this instrument to provide derivative-type curves by A.C. polarography. All potentials quoted are given on the European sign convention. On this convention the potential of the saturated calomel electrode (S.C.E.) has been taken as + 0.246 V *versus* the normal hydrogen electrode (N.H.E.). The electrode employed had a drop time of 3.90 sec and a mass-drop time ($m^{\frac{2}{3}} \cdot t^{\frac{1}{6}}$) value of 1.79 (in water at zero volts applied potential).

Styphnic acid is known to yield three steps of half-waves potentials which vary considerably with pH. PEARSON[2] has reported the half-wave potentials of a number of nitro compounds, including styphnic acid, over a wide range of pH values. Those relating to the three steps due to styphnic acid, determined in an 8% ethanol solution, are summarized in Table I below.

TABLE I

	Styphnic acid half-wave potentials (vs. S.C.E.) in V (PEARSON)		
pH	*1st step*	*2nd step*	*3rd step*
2.0	— 0.07	— 0.12	— 0.23
4.0	— 0.15	— 0.24	— 0.48
6.0	— 0.25	— 0.38	— 0.55
8.0	— 0.38	— 0.66	— 0.82
9.2	— 0.57	— 0.89	— 1.17
10.0	— 0.70	— 1.05	— 1.30

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It was desirable that the present work should be carried out in purely aqueous solution and experiments were therefore conducted over the range of pH 6 to 9 using an aqueous sodium citrate–hydrochloric acid buffer[3]. The results obtained are given in Table II. A typical polarogram is shown in Fig. 1.

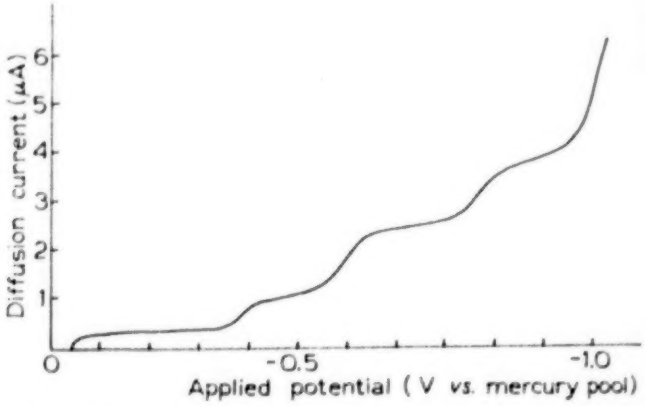

Fig. 1. Styphnic acid in sodium citrate–hydrochloric acid buffer. pH 7.0.

These values were closer to those of PEARSON than might have been expected in view of the changes in reference electrode. It was considered that on this basis the values of Table I could be used as a guide for further work.

TABLE II

	Styphnic acid half-wave potentials (vs. mercury pool) in V		
pH	*1st step*	*2nd step*	*3rd step*
6.0	−0.18	−0.33	−0.60
7.0	−0.38	−0.72	−0.95
9.0	−0.52	−0.92	−1.30

Lead reduces reversibly in aqueous solutions of all the common base electrolytes. It was not considered necessary to obtain half-wave potential values over the range pH 2 to 9 in this solution since the values listed by LINGANE[4], (see Table III) provide sufficient data on which to base predictions of the behaviour of this element under the above conditions.

TABLE III

Base electrolyte	*Lead half-wave potential (V vs. S.C.E.)*
0.1 *N* hydrochloric acid	−0.396
N hydrochloric acid	−0.435
0.5 *M* tartrate pH 4.5	−0.48
0.5 *M* tartrate pH 9.0	−0.50
N sodium hydroxide	−0.755

It was evident from the values quoted in the above tables that separation of the wave due to the lead from those of styphnic acid would be greatest at pH values of 2 or below. At all values above this interference occurs with one or other styphnic acid step. A solution containing $8.8 \cdot 10^{-5}$ *M* lead styphnate in sodium citrate–hydrochloric acid buffer of pH 1.8 and containing 0.005% proteose peptone (maximum suppressor) was therefore prepared and polarographed. The polarogram obtained, which consisted of a large "styphnate" step followed by a smaller step, due to lead, is shown in Fig. 2.

Examination of the polarographic wave of Fig. 2 indicated that the first step was composite and probably contained the three styphnate steps which usually occur. In order to check this the Ilkovic equation was used to obtain a value for *n*, the number of electrons transferred in the reduction. For this purpose the limiting diffusion current was taken as 6.8 μA and the concentration of styphnate ion as $8.8 \cdot 10^{-2}$ mmoles. The value of the mass drop time of the electrode ($m^{\frac{2}{3}} \cdot t^{\frac{1}{6}}$) in this solution at −0.3 V was found to be 1.81. No value for the diffusion coefficient of the styphnate ion is known but, by analogy with similar compounds, it was assumed to be $0.5 \cdot 10^{-5}$ cm^2 sec^{-1}. The value obtained for "*n*" by this calculation was 31.5, indicating that this reduction is highly irreversible. KOLTHOFF AND LINGANE[5] have reported values of 6, 12 and 17 electrons transferred for the first, second and third steps of styphnic acid respectively, giving a total of 35 electrons transferred. The value obtained above is in agreement with this and supports the suggestion that all three waves are combined in the styphnate step obtained by us at pH 1.8.

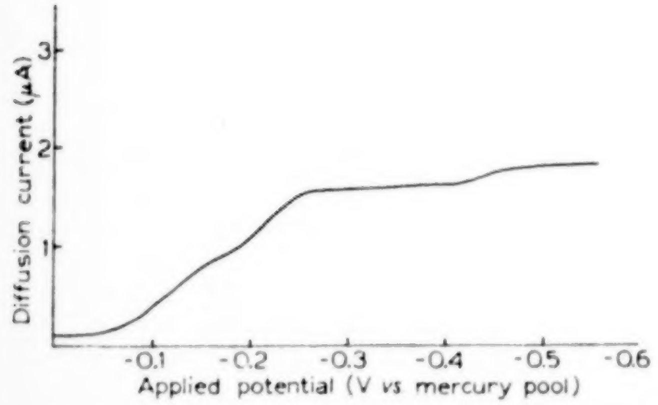

Fig. 2. D.C. Polarogram: lead styphnate $8.8 \cdot 10^{-5}$ *M* in sodium citrate–hydrochloric acid buffer. pH 1.8.

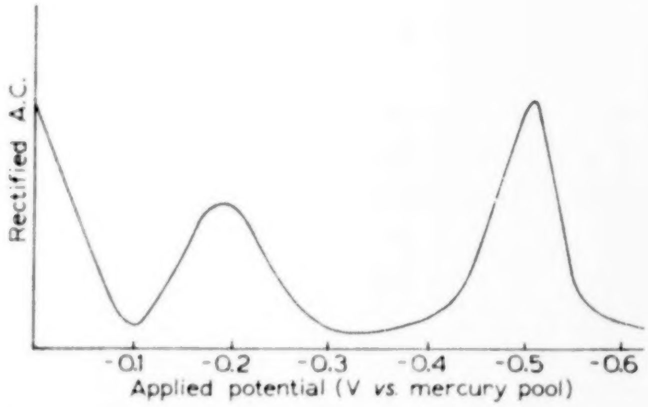

Fig. 3. A.C. Polarogram: lead styphnate $8.8 \cdot 10^{-5}$ *M* in sodium citrate–hydrochloric acid buffer. pH 1.8.

The ratio of the step height due to lead to that due to styphnate was 1:9 and since the styphnate wave preceded the lead it was not possible to obtain a sufficiently large and undistorted lead step. In order to overcome this difficulty it was decided to take advantage of the irreversible nature of the styphnate wave as it was known[6] that polarography of irreversible systems by the A.C. superimposition method gives rise to relatively much smaller peaks than those due to reversible reactions at similar concentration. Polarography of the above solution was therefore repeated using the Cambridge Univector attachment set for A.C. working. The wave obtained is shown in Fig. 3. On this polarogram it is seen that the large styphnate step obtained on normal working (Fig. 2) has become a broad peak characteristic of an irreversible reduction. The lead step has been converted to a well-defined, sharp peak of greater height than that due to the styphnate ion.

It was considered that, on the basis of the above results, a determination of both lead and styphnate ions in the same solution could be made by carrying out polarography on normal and derivative working successfully and following method was therefore prepared.

METHOD

Place 14 ml of a sodium citrate-hydrochloric acid buffer of pH 1.8 (note 1) in a 25-ml graduated flask and add 0.5 ml of 0.1% proteose peptone in 0.2% phenol solution (maximum suppressor) and 10 ml of the sample solution (note 2). Make up to volume with water.

Transfer an aliquot of the prepared solution to a polarographic cell, deoxygenate for 5 min by bubbling hydrogen or nitrogen through it and record the following two polarograms at 25°, using a Cambridge pen writing polarograph equipped with a Univector unit (note 3).

1. A polarogram on normal working over the voltage range 0.0–0.7 V using the mercury pool as anode. Measure the height of the extended wave which occurs over the range −0.1 to −0.3 V.

   Calculate the concentration of styphnic acid by reference to graph 1, prepared as described under "*Calibration*" below, making the appropriate corrections for the sensitivity setting of instrument.
2. A polarogram, with the Univector set for A.C. working, over the range 0.0 to −0.7 V using the mercury pool as anode.

   Measure the height of the peak which occurs at about −0.5 V.

   Calculate the concentration of lead by reference to graph 2, prepared as described under "*Calibration*" below, making the appropriate correction for the sensitivity setting of the instrument.

Calibration

Prepare an aqueous solution of lead styphnate containing 0.6 g/l (note 4). Carry out four determinations as described in the method, using aliquots of 0, 3, 7 and 10 ml respectively of the prepared lead styphnate solution instead of the sample. Measure the wave and peak heights due to the styphnic acid and lead obtained with each solution. Plot calibration graphs of:

1. Styphnic acid step height against the concentration given in Table IV column 3.
2. Lead peak height against the concentration given in Table IV column 4.

TABLE IV

Lead styphnate added (ml)	*Concentration (g/l)*		
	Lead styphnate	*Styphnic acid*	*Lead*
0	0.0	0.0	0.0
3	0.072	0.039	0.033
7	0.168	0.091	0.077
10	0.240	0.130	0.110

Notes

1. The buffer solution is prepared by dissolving 21 g of citric acid in water, adding 200 ml of *N* sodium hydroxide. 5 ml of this solution is titrated with 0.1 *N* hydrochloric acid until the pH is 1.8. This gives a final volume of about 20 ml.
2. The volume of the sample solution may be varied if the concentration of lead styphnate is such that the step heights obtained fall outside the calibration ranges.
3. The Univector Unit produces derivative-type waves by the method of A.C. superimposition. Derivative circuits not of this type are unsuitable for this determination.
4. This compound is a highly sensitive explosive. Great care in handling is necessary.

TRIAL OF THE METHOD

In order to study the accuracy and reproducibility of the method detailed above a number of determinations were made on solutions containing varying amounts of lead and styphnic acid. The results obtained are given in Table V below.

TABLE V

Solution	*Styphnic acid (mg per 25 ml)*		*Lead (mg per 25 ml)*	
	Added	*Found*	*Added*	*Found*
A	3·24	3·3	2·76	2·8
	3·24	3·3	2·76	2·75
	3·24	3·4	2·76	2·8
B	3·24	3·4	3·26	3·4
	3·24	3·2	3·26	3·2
	3·24	3·2	3·26	3·35
C	3·74	3·75	2·76	2·8
	3·74	3·9	2·76	2·85
	3·74	3·7	2·76	2·85

CONCLUSIONS

The results given in Table V show that both lead and styphnic acid can be determined in the same solution, when either are in excess of the stoichiometric amounts corresponding to lead styphnate. Recoveries should be better than ± 5%.

The method of determination of an organic radical and a metal ion in the same solution by successive applications of direct and A.C. polarography is novel and should have wide application, with consequent avoidance of separation procedures.

SUMMARY

A study of the polarographic behaviour of lead styphnate has been made. It has been shown that by use of a combination of normal polarography and derivative polarography using an alternating current method it is possible to determine both lead and styphnate ions in the same solution.

RÉSUMÉ

Une étude du comportement polarographique du styphnate de plomb a été effectuée. En combinant la polarographie normale et une polarographie à courant alternatif, il a été possible de doser le plomb et les ions styphnates dans une même solution.

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ZUSAMMENFASSUNG

Blei- und Styphnat Ionen lassen sich in der gleichen Lösung bestimmen durch Anwendung einer Kombination von normaler Polarographie und Polarographie mit Wechselstrom.

REFERENCES

[1] G. F. REYNOLDS, *Research London*, 9 (1956) 170.
[2] J. PEARSON, *Trans. Faraday Soc.*, 45 (1949) 197.
[3] B. E. CONWAY, *Electrochemical Data*, Elsevier Publishing Cy, 1952, p. 206.
[4] J. J. LINGANE, *Ind. Eng. Chem., Anal. Ed.*, 15 (1943) 583.
[5] I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Vol. II, Interscience Publ., Inc., New York, 1952, page 761.
[6] B. BREYER AND S. HACOBIAN, *Australian J. Chem.*, 7 (1954) 225.

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SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM

II. SULPHANILIC ACID AS A REAGENT

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In our previous communication[1], we have fully discussed the nature, stability and the analytical aspects of the colour reaction that traces of osmium, in different valency states, give with anthranilic acid in faintly acid medium. In this paper, the results of similar studies on the colour reaction between osmium and sulphanilic acid in acid medium, have been recorded.

In both the hexavalent and octavalent state, osmium reacts in the pH range 1.8–3.5 with an excess of sulphanilic acid to form a stable dark-violet complex with an absorption maximum at 490 mμ.

The results obtained on applying the method of continuous variations and the molar ratio method to determine the composition of the complex, indicated that in the case of osmium(VI) the complex is formed when the ratio between the moles of metal and reagent is 1 : 2; in the case of osmium(VIII), however, no definite indication as to the ratio was observed. This may be due to the fact that osmium(VIII) has oxidising properties, so that it slowly oxidises the entire reagent when this is present in small quantities. That the coloured products obtained from osmium(VI) and osmium(VIII), in the presence of an excess of the reagent, are the same is evident from their identical colour reaction, same region of maximum absorption and similar tolerance to pH variation.

The osmium(VI) complex is stable in water and alcohol, and has an average dissociation constant of $1.2 \cdot 10^{-7}$.

In the tetra-, tri- and bi-valent states, osmium does not react with the reagent.

EXPERIMENTAL

Apparatus

All O.D. measurements were carried out with a Hilger Uvispek Spectrophotometer, using a tungsten filament lamp and quartz absorption cells of 1-cm thickness.

A Cambridge pH indicator was used for all pH measurements.

Standard osmium solutions

A standard stock solution of osmium(VIII) was prepared from a 0.1-g ampoule of osmic acid (OsO_4) of Dr. THEODOR SCHUCHARDT, according to the method reported in the previous communication[1].

A standard solution of osmium(VI) was obtained by reducing a 10^{-3} *M* stock solution of osmic acid in a measuring flask with 1 : 2 alcohol (v/v), adding 0.1 ml alcohol for every 10 ml of stock solution, and then making up volume with distilled water. When not in use, this solution was kept in a refrigerator where it was found to be stable for about a fortnight.

Reagent solution

A 1% solution of sulphanilic acid was prepared by suspending in water 1 g of B.D.H. AnalaR grade reagent and dissolving it by the addition of the required quantity of sodium carbonate. When the reagent was completely dissolved, the solution was made up to 100 ml with distilled water.

Buffer solution

Buffer solutions with pH values ranging from 3.42-5.89 were obtained by mixing 0.2 *N* acetic acid and 0.2 *N* sodium acetate in different proportions.[2]

Other reagents

Test solutions of palladium(II), ruthenium(III), rhodium(III), platinum(IV) and iridium(IV) were prepared by the methods reported previously[1].

All other metal solutions were prepared by dissolving their analytical grade chlorides, sulphates, nitrates or oxides in water or hydrochloric acid.

Absorbance curves

For osmium(VI) or osmium(VIII), the colour was developed by adding osmate (OsO_4^{-2}) or osmium tetroxide solution, respectively, to 5 ml of the reagent solution in a 25-ml flask. After allowing the mixture to stand for 2 h it was made up to volume with sodium acetate–acetic acid buffer of pH 3.42. The optical density of the solution was then measured against a reagent blank prepared in the same way, but omitting the osmium.

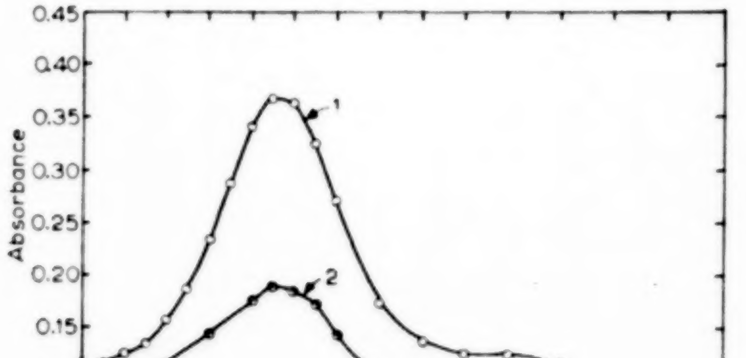

Fig. 1. Absorbance curves for sodium sulphanilate and its osmium complex at pH 3.4. Curve 1: 3.97 p.p.m. osmium(VIII) + 5 ml of 1% reagent. Curve 2: 3.87 p.p.m. osmium(VI) + 5 ml of 1% reagent.

Optical density–wavelength curves of osmium(VIII) and osmium(VI) against the reagent blank, and of the reagent against water at the same pH are represented in Fig. 1. For both the valence states, the colour of the solutions and the nature of the absorption spectra are the same and both show maximum absorption at 490 mμ. In this region the reagent has negligible absorption. Hence an excess of the reagent does not appreciably increase the absorbance of the solution. The depression of the peak in the case of osmium(VI) is due to the presence of alcohol in the solution.

Effects of pH, reagent and time

The pH's of the solutions, prepared by mixing a definite amount of osmium with an excess of the reagent, were adjusted to different values (3.4–5.9) with sodium acetate–acetic acid buffer. Higher and lower pH values were obtained by adding sodium hydroxide and sulphuric acid, respectively. It was found that with increasing pH the optical density of the solutions increased up to pH 1.8 and then remained constant up to 3.5, after which it decreased continuously up to pH 10. Therefore all subsequent measurements were carried out in the pH range 1.8–3.5.

5 ml of the reagent solution were required for maximum development of colour with either 0.5 to 8 p.p.m. of osmium(VIII) or 1 to 18 p.p.m. of osmium(VI). Addition of more reagent did not appreciably alter the density of the colour.

The colour developed very rapidly with the reagent solution, and a stable colour with maximum density was obtained on keeping for 2 h in the cold. The density values of the coloured systems thus produced do not undergo any change even after 24 h. With very dilute solutions of reagent, the colour does not develop at a pH higher than 3.5, even on long standing, but readily does so if a drop or two of dilute sulphuric acid is added to lower the pH to about 1.8 to 3.0.

Beer's law

The complex obeys Beer's law for osmium(VIII) concentrations of 0.5 to 9 p.p.m. and osmium(VI) concentrations of 1 to 18 p.p.m. (*cf.* Fig. 2), when measurements are made against a reagent blank.

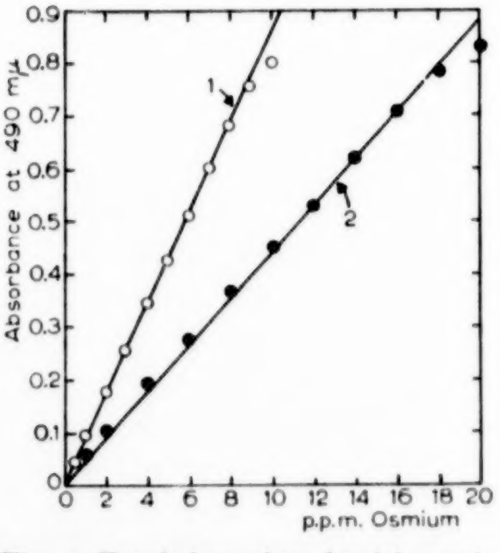

Fig. 2. Beer's law plots for (1) osmium(VIII) and (2) osmium(VI); pH 3.4.

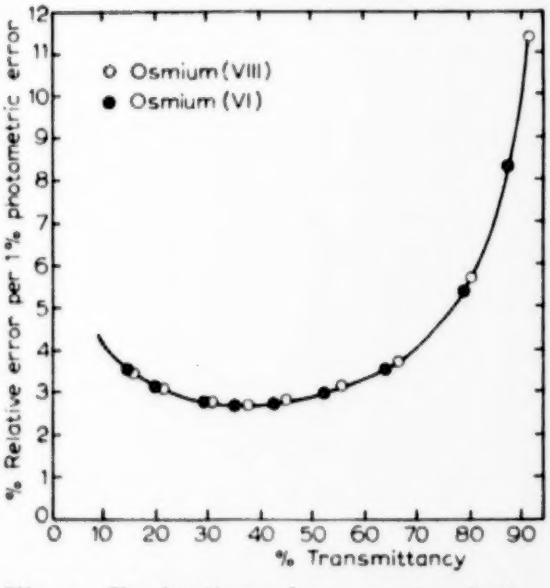

Fig. 3. Evaluation of per cent relative error ($dc/c \times 100$) relative to 1% absolute photometric error.

Optimum range and accuracy

The % relative error per 1% absolute photometric error was calculated by means of the equation reported previously[1], and plotted against transmittancy (Fig. 3) to show how the analytical error varies with the transmittancy.

On plotting % absorbancy (100 — % transmittancy) at 490 mμ as the ordinate against log concentration as the abscissa, the optimum concentration ranges were found to be between 2 and 8 p.p.m. of osmium(VIII) and between 4 and 16 p.p.m. of osmium(VI), the curves having the steepest slopes there (Fig. 4). For these regions, the % relative errors per 1% absolute photometric error are 3.02 for osmium(VIII) and 3.1 for osmium(VI), as evaluated by means of the equation described in a previous paper[1].

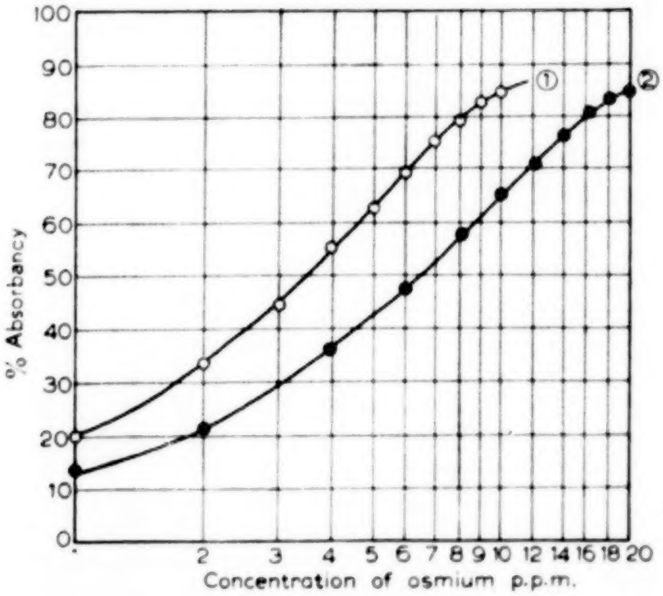

Fig. 4. Calibration curves for (1) osmium(VIII) and (2) osmium (VI) at 490 mμ.

Sensitivity

The spectrophotometric sensitivities, as calculated from Beer's law curves, were found to be 0.01 μg/cm² for osmium(VIII) and 0.02 μg/cm² for osmium(VI) (*cf.* SANDELL[3]).

Effect of diverse ions

To determine the interference of diverse ions, solutions were prepared with 4.2 p.p.m. of osmium(VI), 5 ml of 1% reagent and varying concentrations of each ionic species being tested. An increase or decrease of 0.005 unit in absorbance was taken as an interference. The following ions were found to interfere even in a ratio of 1 : 1 Pd^{+2}, Pt^{+4}, Ru^{+3}, Rh^{+3}, Ir^{+4}, Cu^{+2}, Ag^{+}, Zn^{+2}, Cd^{+2}, Hg^{+2}, Al^{+3}, Th^{+4}, Zr^{+4}, As^{+3}, Sb^{+3}, Cr^{+3}, W^{+6}, U^{+6}, Mn^{+2}, Co^{+2}, Ni^{+2}. It is preferable to separate osmium as osmic acid by nitric acid oxidation and distillation[3] in order to avoid the interference of other ions.

Nature of the complex in solution

Two methods were employed to ascertain the empirical formula of the osmium(VI)-sulphanilic acid complex in solution. These were the method of continuous variations and the molar ratio method, which we have also applied in a previous investigation[1].

The results obtained with these two methods indicate that in solution osmium(VI) forms a 1 : 2 complex with the reagent. As in the case of anthranilic acid[1], difficulties were encountered when excess of osmium and smaller amounts of reagent were present, owing to black osmium dioxide and metallic osmium separating from the solution.

In both methods, solutions of osmium(VI) and the reagent were mixed and treated with two drops of 6 *M* sulphuric acid. After 2 h, when the colour had developed, the volume of the mixed solution was made up to 25 ml with a buffer of pH 3.42. It was then allowed to stand overnight, and afterwards the optical density was measured. With dilute equimolecular solutions, no colour developed until the pH of the mixture had been adjusted to a value between 1.8 and 3.0; further, it was found that for full colour development a period of 24 h was absolutely necessary. Results of such experiments are given in Figs. 5 and 6.

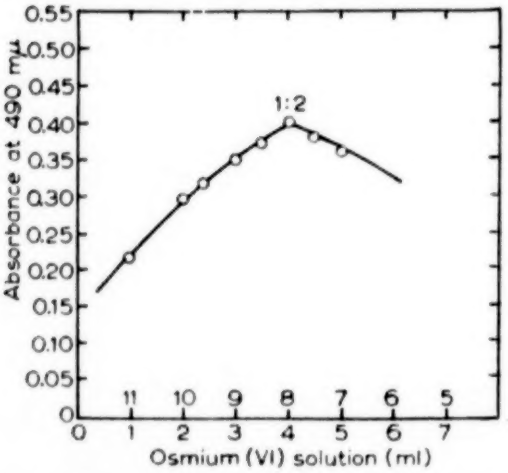

Fig. 5. Determination of the ratio of reagent to osmium(VI) by Job's method. Concn. osmium(VI) = concn. sulphanilic acid (sodium salt) = $0.8935 \cdot 10^{-3}$ *M*.

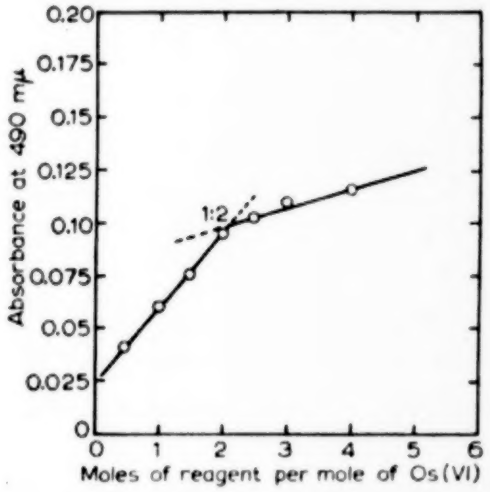

Fig. 6. Determination of ratio of reagent to osmium(VI) by the molar ratio method. Concn. osmium(VI) = concn. sulphanilic acid = $0.8935 \cdot 10^{-3}$ *M*.

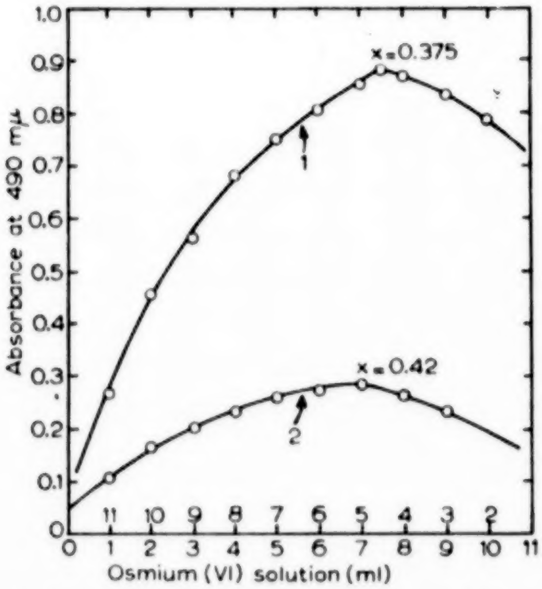

Fig. 7. Absorbance of mixtures of non-equimolecular solutions. Curve 1: $1.15 \cdot 10^{-3}$ *M* osmium(VI) solution, $5.75 \cdot 10^{-3}$ *M* sulphanilic acid (sodium salt) solution. Curve 2: $0.575 \cdot 10^{-3}$ *M* osmium(VI) solution, $2.875 \cdot 10^{-3}$ *M* sulphanilic acid (sodium salt) solution.

Dissociation constant of the osmium(VI)–sulphanilic acid complex

For the evaluation of the dissociation constant of the complex, mixtures of non-equimolecular solutions of reagent and osmate (OsO_4^{-2}) were treated with a drop of 12 *N* sulphuric acid and allowed to stand for 2 h. After making up their volumes to 25 ml with buffer of pH 3.42, their absorbances were measured at 490 mμ. Experimental data are given in Fig. 7 where absorbances have been plotted against the volumes of osmium(VI) solution added. Owing to the higher concentration of the reagent, it was not necessary to let the solution stand overnight for maximum colour development.

From the data obtained (*cf.* Fig. 7) the dissociation constant was calculated, using JOB's equation[1]; it was found to be $1.2 \cdot 10^{-7}$.

ACKNOWLEDGEMENT

Our thanks are due to the University Grants Commission for providing us with funds to purchase the spectrophotometer used in this work.

SUMMARY

Sulphanilic acid has been found to be a very effective reagent for the spectrophotometric determination of hexavalent and octavalent osmium in the pH range between 1.8–3.5. In these two valence states, the element forms a dark-violet complex with the reagent, the absorption maximum of the complex being at 490 mμ. As most of the other ions interfere in the determination, the element must be separated as osmic acid by nitric acid distillation. Beer's law is obeyed in the case of 0.5 to 9 p.p.m. of osmium(VIII) and 1 to 18 p.p.m. of osmium(VI); the optimum concentration ranges are from 2 to 8 p.p.m. for osmium(VIII) and from 4 to 16 p.p.m. for osmium(VI). In these ranges, the % relative errors per 1% absolute photometric error are 3.02 for osmium(VIII) and 3.1 for osmium(VI). Application of the method of continuous variations and the molar ratio method indicates that in solution hexavalent osmium and the reagent form a 1 : 2 complex, with an average dissociation constant of $1.2 \cdot 10^{-7}$.

RÉSUMÉ

L'acide sulfanilique est proposé comme réactif pour le dosage spectrophotométrique de l'osmium(VI) et (VIII). Le complexe formé est violet foncé. La plupart des autres ions gênent; il faut alors séparer l'osmium par distillation.

ZUSAMMENFASSUNG

Als Reagens zur spektrophotometrischen Bestimmung von Osmium(VI) und (VIII) wird Sulfanilsäure vorgeschlagen, die damit einen dunkel-violett gefärbten Komplex bildet. Da die meisten Fremd-Ionen stören, muss das Osmium durch Destillation abgetrennt werden.

REFERENCES

[1] A. K. MAJUMDAR AND J. G. SEN GUPTA, *Anal. Chim. Acta.*, 21 (1959) 532.

[2] A. I. VOGEL, *A Text Book of Quantitative Inorganic Analysis*, Longmans, Green & Co., New York, 1953.

[3] E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, 2nd Ed., Interscience Publ. Inc., New York, 1950.

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THE DETERMINATION OF URANIUM BY SQUARE WAVE POLAROGRAPHY

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INTRODUCTION

Conventional polarography is a useful technique for the determination of uranium, but it is not suitable for very low concentrations. SHALGOSKY[1] used the step from a sulphuric acid–perchloric acid–tartrate supporting electrolyte for the determination of uranium concentrations in the range from 20 to 200 μg/ml. A linear calibration graph of step height against concentration was obtained over this concentration range, but a non-linear graph resulted for lower uranium concentrations.

The advantage of the square wave polarography for the determination of trace amounts of several elements[2] is now well established and a study of the potentialities of this instrument for the determination of very small amounts of uranium was therefore desirable. Brief reference to the determination of uranium by square wave polarography was made by FERRETT AND MILNER[3]. They used a 0.1 N hydrochloric acid supporting electrolyte and reported two peaks at —0.18 and —0.86 V *vs.* the mercury pool anode respectively. The first peak coalesced with a copper peak and was unsuitable for the determination of uranium in the presence of copper. For the determination of traces of uranium in effluents, MILNER AND FERRETT[4] found a molar perchloric acid supporting electrolyte to be most satisfactory. The uranium peak occurred at about —0.55 V *vs.* the mercury pool anode and it proved suitable for the determination of uranium at the level of a few tenths of a microgram per ml of final solution. Any organic matter in the samples was first destroyed by evaporation to fumes of perchloric acid followed by the dropwise addition of conc. nitric acid.

EXPERIMENTAL

In view of the satisfactory results obtained by MILNER AND FERRETT[4] with mineral acid supporting electrolytes for the determination of small amounts of uranium, a more detailed investigation of this type of supporting electrolyte was carried out and the results obtained are summarized below:

(*a*) *Hydrochloric acid*

In studying the behaviour of uranium in this supporting electrolyte, 1-ml aliquots of a standard solution in dilute perchloric acid containing 50 μg of uranium were taken and evaporated just to dryness. Each residue was dissolved in the requisite volume of 10 N hydrochloric acid before dilution to a volume of 5 ml with water. A well-defined peak was obtained from solutions in the range 0.5 to 1.5 M in HCl, and the $E_{\frac{1}{2}}$ value of the peak, as determined by conventional methods, varied with the acid concentration as follows:

Molarity of HCl	0.5	1.0	1.5
$E_{\frac{1}{2}}$ *vs.* S.C.E.	—0.20 V	—0.20 V	—0.196 V

From 2 *N* HCl solutions the definition of the uranium peak was unsatisfactory due to abnormal responses of the instrument. Although the $E_{\frac{1}{2}}$ value of the peak moved to slightly more positive value with increase in the acid concentration, the most important effect was the considerable decrease in the height of the peak (See Fig. 1). From this behaviour strict control of the hydrochloric acid concentration is essential for the use of this peak in quantitative analysis. When this is done, the height of the peak is proportional to the concentration of uranium.

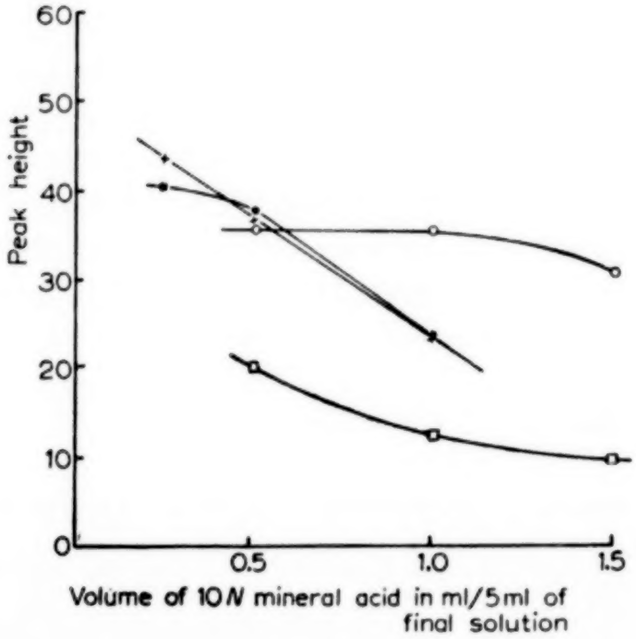

Fig. 1. Influence of the nature and concentration of mineral acid on the peak height for uranium. Tartrate absent. Uranium concentration 10 μg/ml. ○ $HClO_4$; × HCl; ● HNO_3; □ H_2SO_4.

(*b*) *Nitric acid*

Uranium was found to give a well-defined peak in this supporting electrolyte. In experiments to study any possible effects of variations in the nitric acid concentration, 1-ml aliquots of a standard uranium solution in dilute nitric acid containing 50 μg of U per ml were evaporated to dryness. Each residue was dissolved in the requisite volume of 10 *M* nitric acid before dilution to 5 ml with water.

With an increase in the nitric acid concentration the uranyl peak moved to more positive potentials, as shown by the following $E_{\frac{1}{2}}$ values for solutions up to 1.5 *M* in nitric acid:

Molarity of HNO_3	0.25	0.5	1.0	1.5
$E_{\frac{1}{2}}$ *vs.* S.C.E.	—0.235 V	—0.21 V	—0.175 V	—0.16 V

In 1.5 *M* nitric acid solutions the mercury is attacked fairly rapidly and it is necessary to record the polarogram within 30 min of pouring the solution into the cell.

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Over the range examined, the relationship between the half-wave potential and the logarithm of the acid concentration is given by the equation:

$$E_{\frac{1}{2}} = -0.175 - 0.096 \log_{10} \text{(acid concentration)}$$
$$\simeq -0.175 + 0.096 \text{ pH}$$

As in the experiments with hydrochloric acid, the height of the peak decreased appreciably with increase in the nitric acid concentration (See Fig. 1). The acidity of the final solution must therefore be carefully controlled in using this peak in analysis and then the peak height is proportional to the concentration of uranium.

(*c*) *Sulphuric acid*

In a study of this supporting electrolyte the procedure of evaporating the uranium solution to fumes of sulphuric acid before recording the uranyl peak was avoided because of the difficulties experienced by SHALGOSKY[1]. Aliquots (1 ml) containing 50 μg of uranium in 0.1 *M* perchloric acid were taken and mixed with the requisite volumes of 5 *M* sulphuric acid before dilution to 5 ml with water. Under these conditions the height of the uranium peak was much smaller than that for the same concentration of uranium in HCl and HNO_3 solutions respectively (See Fig. 1). The peak height also decreased with increase in sulphuric acid concentration over the range studied. The half-wave potential of the peak became more positive with increase in acidity, in accordance with the following values:

Molarity of H_2SO_4	1.0	2.0	3.0
$E_{\frac{1}{2}}$ *vs.* S.C.E.	−0.205 V	−0.175 V	−0.155 V

Again a linear relationship exists between the $E_{\frac{1}{2}}$ value and the logarithm of the acid concentration and is given by the equation: $E_{\frac{1}{2}} = -0.205 - 0.111 \log_{10}$ (acid concentration).

(*d*) *Perchloric acid*

A well-defined peak was obtained from perchloric acid solutions up to 3 *M* in this acid. Variations in the acid concentration had only a small effect on the peak height and the position of the peak, the $E_{\frac{1}{2}}$ values being as follows:

Molarity of $HClO_4$	1.0	2.0	3.0
$E_{\frac{1}{2}}$ *vs.* S.C.E.	−0.21 V	−0.225 V	−0.23 V

This supporting electrolyte proved to be the only one not requiring careful control of the final acid concentration. The peak height for a concentration of uranium of 10 μg/ml in *M* $HClO_4$ was much greater than that for the same concentration in sulphuric acid, but approximately the same as that in *N* HCl and *M* HNO_3 solutions. Perchloric acid appeared potentially more useful than the others for application in analytical chemistry and was therefore examined in more detail. The relationship of peak height *vs.* concentration was studied over a very wide range of uranium concentrations in *M* $HClO_4$ and was found to be linear over the range from 1 to at least 2,500 μg of uranium per ml of final solution. Small peaks were obtained for uranium concentrations less than 1 μg/ml, but these would not be very suitable for analytical purposes because of the poor precision in measuring such small peak heights.

The effects on the uranium peak of peaks produced by several other elements were examined. Cupric ions give a peak just proceding that for uranium which causes little difficulty for ratios of copper to uranium of 1 : 1. Serious interference occurs, however, for higher ratios. Lead gives a peak following the uranium peak which is less troublesome than the copper peak. The peak for bismuth occurs very close to the uranium peak and the resolution of these peaks is very poor for bismuth to uranium ratios of 1 : 1. Similarly molybdenum gives an interfering peak with an $E_{\frac{1}{2}}$ value of —0.20 V *vs.* S.C.E. in M $HClO_4$. Several elements, including Ni, Mn and ferric iron, cause no interference.

ACIDIC–TARTRATE SUPPORTING ELECTROLYTES

This type of supporting electrolyte was studied because of the interferences occurring with the uranium peak in the perchloric acid solutions. From results in conventional polarography, mineral acid–tartrate[1] and –oxalate[5] supporting solutions appeared to be the most suitable for the removal of interferences in the polarographic determination of uranium. SHALGOSKY, for example, recommended a sulphuric acid–perchloric acid–tartrate supporting electrolyte and concluded that the addition of tartrate assisted mainly in the separation of interfering steps from the uranium step and hardly affected the diffusion current or the mechanism of the reaction at the dropping mercury electrode. From this supporting electrolyte the steps for copper, bismuth and lead were well-separated from the uranium step. However, the step height–concentration graph was not linear for low uranium contents.

In the investigations of the suitability of the tartrate base for the determination of uranium by square-wave polarography, a solution of the supporting electrolyte was prepared by dissolving 6 g of sodium tartrate and 0.15 g of sodium chloride in water followed by dilution to a volume of 50 ml. A standard uranium solution was prepared by dissolving 100 mg of U_3O_8, previously ignited at 800°, in about 2 ml of hot concentrated perchloric acid (60%). After cooling, the solution was transferred to a 100-ml volumetric flask and diluted to volume with water. Suitable dilutions of this standard solution were made, perchloric acid being added as required to maintain the solutions about 0.1 M with respect to this acid. Results obtained on investigating solutions of this tartrate supporting electrolyte in conjunction with different mineral acids are summarized below:

(*a*) *Hydrochloric acid–tartrate*

In the study of the hydrochloric acid supporting electrolyte, a well-defined peak was obtained for uranium in solutions molar in this acid and these conditions were therefore used to investigate the effects of different tartrate concentrations. Aliquots of the standard uranium solution containing 50 μg of this element were taken and evaporated to remove perchloric acid. Then the requisite volume of the tartrate base was added and the solution warmed. After cooling, 0.5 ml of 10 N hydrochloric acid was added and the solution diluted to 5 ml with water. With volumes of tartrate base varying from 0 to 2.0 ml, negligible effect was obtained on the peak height and also on the position of the peak. In experiments to study the effect of hydrochloric acid concentration, the volume of tartrate solution was fixed at 0.5 ml and varying amounts of 10 *N* HCl were added after the tartrate, as before. Abnormal instrumental responses were obtained from solutions 2 *M* in HCl, but in the range from 0.5 to 1.5 *M* well-defined peaks were obtained, the peak height decreasing appreciably with increase in acidity (See Fig. 2). Changes in acidity had little effect upon the half-wave potential of the peak, as shown by the following values:

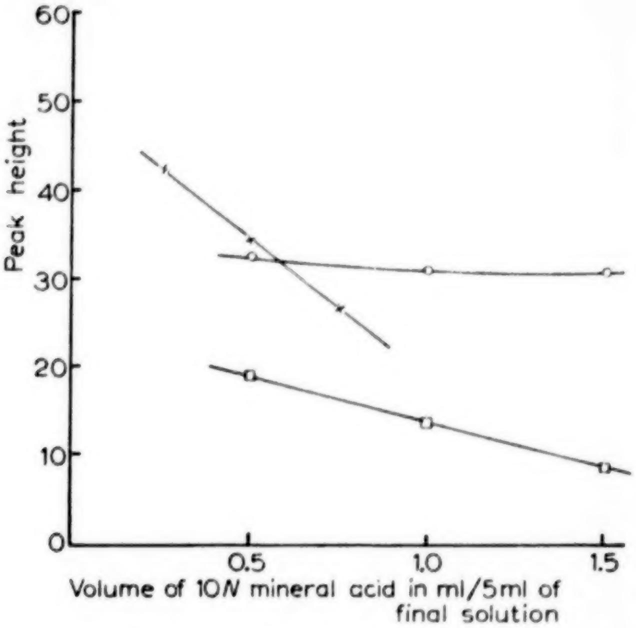

Fig. 2. Influence of the nature and concentration of mineral acid in an acid–tartrate supporting electrolyte on the peak height for uranium. Tartrate present. Uranium concentration 10 μg/ml. o $HClO_4$; × HCl and HNO_3; □ H_2SO_4.

Molarity of HCl	0.5	1.0	1.5
$E_{\frac{1}{2}}$ *vs.* S.C.E.	−0.21 V	−0.205 V	−0.20 V

The close similarity between these values and those for HCl alone suggests that the same species is being reduced with or without the presence of tartrate. The quantitative behaviour of this peak was studied in solutions containing 0.5 ml of tartrate solution and 0.5 ml of 10 *N* HCl in 5 ml of final solution. A linear relationship was obtained between peak height and uranium concentration over the range from 5 to at least 20 μg of uranium per ml of final solution. Very unsatisfactory results were obtained, however, for concentrations less than 5 μg/ml. The peak was incompletely developed and the base line was unstable.

(*b*) *Nitric acid–tartrate*

The effects of acidity and tartrate concentration on the uranyl peak in this supporting electrolyte proved to be very similar to those occurring in HCl–tartrate solutions. In experiments with varying amounts of tartrate base, 0.5 ml of 10*M* nitric acid was included in 5 ml of final solution. As before, variations in the volume of tartrate solution from 0.5 to 2.0 ml had negligible influence on the peak height and the position of the peak remained fairly constant. Similarly, in experiments to study the influence of the nitric acid concentration, the volume of tartrate solution was kept constant at 0.5 ml in 5 ml of final solution. The peak height for 50 μg of uranium decreased appreciably with increase in acidity from 0.5 to 1.5 M and strict control of acidity must therefore be enforced in applying this supporting electrolyte to analytical determinations. The half-wave potential of the peak moved to slightly more positive potentials with an increase in acidity, according to the following results:

Molarity of HNO_3	0.5	1.0	1.5
$E_{\frac{1}{2}}$ *vs.* S.C.E.	−0.21 V	−0.205 V	−0.19 V

The $E_{\frac{1}{2}}$ value in the 0.5 M HNO_3–tartrate solution agrees with that in the 0.5 M HNO_3 supporting electrolyte. This suggests that the same uranium species is reduced at the dropping mercury electrode in each case. It is significant that an increase in the nitric acid concentration has a smaller effect in the presence of tartrate than in its absence.

The quantitative behaviour of the peak was studied on maintaining the volume of tartrate solution and 10 M HNO_3 each at 0.5 ml per 5 ml of final solution. As with HCl–tartrate solutions, a linear relationship was obtained on plotting peak height against concentration over the range 5 to 20 μg of uranium per ml. The peaks for smaller concentrations of uranium were also completely developed, a linear calibration graph being obtained over the range 0.5 to 2.0 μg of uranium per ml.

(*c*) *Sulphuric acid–tartrate*

The influence of the tartrate concentration on the uranium peak was investigated with the H_2SO_4 concentration fixed at 1 ml of 5 M acid per 5 ml of final solution. The peak height remained fairly constant for amounts of tartrate from 0.5 to 2.0 ml and there was negligible influence on the position of the peak. In studying the effect of H_2SO_4 concentration, experiments were carried out with the volume of tartrate solution constant at 0.5 ml. As before the peak height depended on the H_2SO_4 concentration and decreased appreciably with an increase in acidity (see Fig. 2). There was also some loss in sensitivity in this solution as compared with the other acidic–tartrate supporting electrolytes. The half-wave potential value of the peak moved to slightly more positive potentials with an increase in acidity, according to the following values:

Molarity of H_2SO_4	1.0	2.0	3.0
$E_{\frac{1}{2}}$ *vs.* S.C.E.	−0.20 V	−0.20 V	−0.185 V

With this supporting electrolyte, the half-wave potential value in 1 M H_2SO_4 is the same as that measured in the absence of tartrate. Again an increase in acidity has a smaller effect in these solutions than in supporting electrolytes containing only sulphuric acid.

On using 0.5 ml of tartrate solution and 1 ml of 5 M H_2SO_4 per 5 ml of final solution, quantitative peaks were obtained for uranium concentrations in the range 5 to 20 μg/ml. For lower uranium concentrations fully-developed peaks were produced, but the maximum sensitivity of the instrument had to be used and some interference from variations in the capillary response results.

(*d*) *Perchloric acid–tartrate*

With the volume of tartrate solution constant at 0.5 ml per 5 ml of final solution, the height of the uranyl peak was found to be fairly constant in solutions ranging from 1 to 3 *M* in $HClO_4$. Also the shift in the half-wave potential was insignificant in the range covered:

Molarity of $HClO_4$	1.0	2.0	3.0
$E_{\frac{1}{2}}$ *vs.* S.C.E.	—0.225 V	—0.23 V	—0.225 V

On studying the effect of varying the tartrate concentration, all solutions were adjusted to be 2 *M* in $HClO_4$ and for variations of tartrate from 0.5 to 2.0 ml, the height of the peak showed negligible variation. The quantitative behaviour of the uranium peak was studied in solutions containing 1 ml of 10 *M* $HClO_4$ and 0.5 ml of tartrate solution per 5 ml of final solution. Linear calibration graphs of peak height against concentration were obtained over the concentration range from 0.6 to at least 50 μg per ml. A second uranium peak occurring at about —1.2 V *vs.* the mercury pool anode was also observed in this supporting electrolyte, but it suffered some interference probably from the reduction of hydrogen ions at the cathode.

This supporting electrolyte appeared to be the most useful of the acid–tartrate solutions studied for the determination of uranium and the behaviour of other elements and it was therefore examined in some detail. Bismuth was studied first because of the serious interference caused by this element to the uranium peak in perchloric acid solutions. Bismuth ions gave a peak in a 1 *M* $HClO_4$–tartrate solution with an $E_{\frac{1}{2}}$ value of —0.024 V *vs.* S.C.E. and well separated from the uranium peak (see Fig. 3). Moreover, the $E_{\frac{1}{2}}$ value shifted to slightly more positive values with increase in the acid concentration. The peak for copper in this supporting electrolyte occurred at a still more positive potential. Also the half-wave potential for the reduction of ferric iron occurred at a potential more positive than +0.10 V *vs.* S.C.E. Interference from any of these elements in the uranium determination would only occur with very high ratios of each element to uranium.

Molybdate ions gave a peak at —0.19 V *vs.* S.C.E. in a *M* $HClO_4$–tartrate solution. This peak caused serious interference with the uranyl peak, even for low concentrations of molybdenum. Similarly the reduction of vanadic ions gave an interfering peak at —0.15 V *vs.* S.C.E. A peak for chromic ions occurred at —0.43 V *vs.* S.C.E. and difficulties resulted in the determination of uranium for high unfavourable ratios of chromium to uranium. Similar conclusions apply to lead which give a peak at about the same potential. Elements found to cause no interference include zinc, nickel, cadmium, indium, cobalt and manganese.

ANALYTICAL APPLICATION OF THE URANIUM PEAK IN THE PERCHLORIC ACID–TARTRATE SUPPORTING ELECTROLYTE

Mineral analysis — Determination of uranium

The determination of the uranium content of minerals is frequently required and several methods of analysis are already available. A neutron activation method[6] is available for laboratories with facilities for radiochemical work. In chemical methods for this determination, preliminary separation and concentration of the uranium is required before the determination is completed either polarographically or absorptiometrically[7,8]. The chromatographic method of separation is usually employed and the step for uranium from an acidic oxalate or acidic tartrate supporting electrolyte is used in the polarographic determination. It was considered that the application of the square-wave polarograph instead of the conventional polarograph might improve this determination. With the improved sensitivity of this instrument, it should be possible to eliminate the lengthy separation and concentration of the uranium and experiments were therefore carried out to investigate the applicability of the uranium peak from the tartrate–perchloric acid supporting electrolyte to the direct determination of the uranium content of minerals.

The most reliable method for producing the solution of mineral samples involves sintering with sodium peroxide followed by extraction into water. After this solution procedure it would be necessary to destroy any peroxide in the aqueous extract before proceeding with the polarographic determination because of the interfering reduction of peroxide at the dropping mercury electrode. Preliminary experiments showed that, if the aqueous extract of sodium peroxide used in a sinter was acidified with hydrochloric acid and then evaporated to dryness, decomposition of the peroxide took place rapidly. After re-solution of the salts, aliquots of the resultant solution were evaporated to fumes of perchloric acid before the addition of the tartrate supporting electrolyte. Normal polarographic traces were obtained without any indication of interference from the reduction of peroxide. The polarograms showed a peak for lead present as an impurity in the sodium peroxide, but no peaks or irregularities in the applied voltage range for the uranium peak. Based on these findings, a direct procedure was developed for the analysis of minerals for uranium and further details are as follows:

Procedure for uranium in minerals

Transfer 100 mg of finely-ground sample to a small platinum crucible and intimately mix with 0.8 g of pure sodium peroxide (B.D.H. micro reagent grade). Cover the mixture with a further 0.2 g of sodium peroxide and place the crucible in a muffle furnace at 480 ± 20° for 20 min. After cooling, detach the peroxide sinter from the crucible and dissolve in a small volume of water. Add 10 ml of hydrochloric acid ($d = 1.18$) to the aqueous solution in the beaker and heat to boiling on a hot plate. Gradually evaporate the solution to dryness, using infra-red heating to complete the evaporation. Then bake for about 20 min on a hot plate to dehydrate the silica. Redissolve the salts in 20 ml of hydrochloric acid ($d = 1.18$) with boiling and then dilute with an equal volume of water. Filter the cooled solution through a Whatman No. 40 filter paper, washing with dilute hydrochloric acid and collecting the filtrate in a 100-ml volumetric flask (see Note). Dilute the solution to volume, then transfer 5 ml to a small beaker followed by 1 ml of 10 N perchloric acid (lead-free) and evaporate the solution just to fumes of perchloric acid. Rinse the beaker sides with a small volume of water and again evaporate the solution just to fumes of perchloric acid. To the cooled solution add 0.50 ml of the tartrate supporting electrolyte and dilute to 5 ml in a volumetric flask with water. After mixing, transfer this solution to a polarograph cell, de-aerate and record the uranium peak by scanning from —0.1 to —0.6 V *vs.* the mercury pool anode. Then make an addition of a standard uranium solution, de-aerate and record the peak.

Note. If the silica content of the sample is high, transfer the filter paper plus contents to a platinum dish and ignite. Add 2–3 drops of concentrated sulphuric acid to the residue, followed by a few ml of hydrofluoric acid and evaporate to remove silica. Then heat to remove the sulphuric acid and continue heating until no more fumes of this acid are visible. Dissolve any residue in hydrochloric acid and add to the main sample solution before dilution to 100 ml with water.

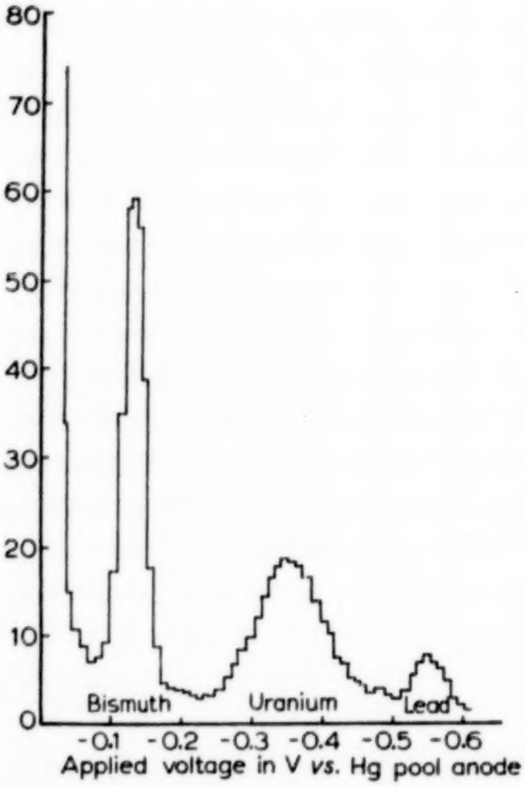

Fig. 3. Polarogram of bismuth, uranium and lead in the 2 N $HClO_4$–tartrate supporting electrolyte.

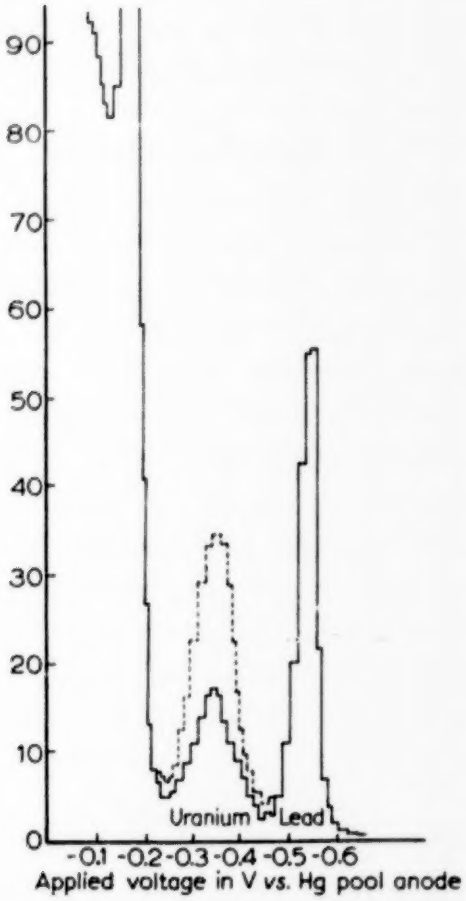

Fig. 4. Polarogram for monazite sand sample.- - - - - -: after standard addition of uranium.

Results

The suitability of this procedure was tested on samples which had been analysed by other methods and the results are given in Table I. Samples 1 and 2 were produced in the mineral dressing study of a quartz–iron oxide ore containing small amounts of pyrites, marcasite, sphalerite, galena, pitchblende and mica. The results for uranium reported in the last column were obtained by conventional polarography after the separation of the uranium from other sample constituents by paper chromatography. The remaining samples in Table I were pitchblende and monazite samples previously analysed for uranium by the neutron activation method. Fairly good agreement was obtained between the results by direct polarography and those by other methods. The square-wave polarographic method proved fairly rapid compared with the other methods for this determination, because chemical separations were unnecessary on the samples examined. A typical polarogram for a monazite sample is given in Fig. 4.

TABLE I

RESULTS FOR URANIUM IN MINERALS BY SQUARE-WAVE POLAROGRAPHY

Nature of sample	*Uranium %*	
	By square-wave polarography	*By other methods*
1. Quartz–iron oxide	0.295	0.29
2. Quartz–iron oxide	0.295	0.31
3. Pitchblende–dunite	0.093	0.097, 0.093, 0.10
4. Pitchblende–dunite	0.017	0.02, 0.018
5. Monazite–dunite	0.034	0.038
6. Monazite	0.28	0.30, 0.29

ACKNOWLEDGEMENT

Thanks are due to Mr. J. M. Hale for carrying out many of the halfwave potential measurements.

SUMMARY

Mineral acid supporting electrolytes, both in the presence and absence of tartrate ions, have been examined for use in the determination of small amounts of uranium by square wave polarography. A perchloric acid–tartrate supporting electrolyte is most suitable for analytical work and has been used for the determination of uranium in mineral samples.

RÉSUMÉ

Les auteurs ont examiné divers acides minéraux, comme électrolytes de base pour le dosage de l'uranium par polarographie ,,square-wave''. L'acide perchlorique, en présence de tartrate est recommandé. Une méthode est proposée pour le dosage de l'uranium dans ses minéraux.

ZUSAMMENFASSUNG

Die Anwendbarkeit der ,,square-wave'' Polarographie auf die Bestimmung von Uran in Gegenwart von verschiedenen Mineralsäuren als Elektrolyte wurde untersucht. Perchlorsäure unter Zusatz von Tartrat ist besonders geeignet und wurde zur Bestimmung von Uran in Mineralien angewandt.

REFERENCES

[1] H. I. Shalgosky, *Analyst*, 81 (1956) 512.
[2] G. W. C. Milner and L. Slee, *Ind. Chemist*, 33 (1957) 494.
[3] D. J. Ferrett and G. W. C. Milner, *Analyst*, 80 (1955) 132.
[4] G. W. C. Milner and D. J. Ferrett, *unpublished work*.
[5] D. I. Legge, *Anal. Chem.*, 26 (1954) 1617.
[6] A. A. Smales, *Analyst*, 77 (1952) 778.
[7] G. W. C. Milner, *Principles and Applications of Polarography and other Electroanalytical Processes*, *Longmans, Green & Co. Ltd.*, *London*, 1957.
[8] J. A. S. Adams and W. J. Maeck, *Anal. Chem.*, 26 (1954) 1635.

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POLAROGRAPHIC DETERMINATION OF MIXTURES OF ALUMINUM AND GALLIUM

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INTRODUCTION

Aluminum and gallium, when present together, are difficult to determine quantitatively. COLLAT AND ROGERS[1] have proposed a fluorometric method for determining microgram quantities from mixtures of the oxinates in chloroform solution. WILLARD AND DEAN[2] have introduced a polarographic method for determining aluminum using the di-*o*-hydroxyazo dye, Pontachrome Violet SW (C.I. 169), which is the sodium salt of 5-sulfo-2-hydroxy-α-benzene-azo-2-naphthol. These investigators observed that reaction between the dye and aluminum(III) resulted in a new wave, the diffusion current of which was directly related to the concentration of aluminum present. This method can be used to determine $8 \cdot 10^{-6} M$ to $2.2 \cdot 10^{-4} M$ aluminum within 5%. The method has been further studied by PERKINS AND REYNOLDS[3]. LATIMER AND HOUSTON[4] showed that the chelate of Pontachrome Violet SW with gallium(III) has similar polarographic behavior. The diffusion current of the chelate reduction wave is a linear function of gallium in solution. They determined $1.4 \cdot 10^{-5} M$ to $1.4 \cdot 10^{-4} M$ gallium by this method. SAYLOR AND CASTOR[5] developed an amperometric method for the determination of fluoride using the reactions of aluminum with Superchrome Garnet Y (C.I. 168), the sodium salt of 5′-sulfo-2,4,2′-trihydroxyazobenzene. ADCOCK[6] used the polarographic reduction of the aluminum-Superchrome Garnet Y chelate to determine concentrations of aluminum from $2 \cdot 10^{-6} M$ to $3 \cdot 10^{-3} M$. Gallium also reacts with Superchrome Garnet Y(SGY) giving similar polarographic behavior[7]. However, in addition to the usual two waves observed for the aluminum–SGY system, the gallium–SGY system produces a third polarographic wave having a halfwave potential of approximately -1.05 V *versus* the saturated calomel electrode. The diffusion current of the third wave is also a linear function of the concentration of gallium present, but it is considerably smaller than that of the more positive chelate wave.

The work described here was undertaken to provide a polarographic method for determining mixtures of aluminum and gallium as part of a more general study of aluminum, gallium, and indium chelates of azo compounds.

EXPERIMENTAL AND RESULTS

Apparatus and procedure

A Sargent polarograph, Model XXI, was used to obtain all current–voltage curves. All potentials were referred to the saturated calomel electrode (S.C.E.). Measurements of pH were made to ± 0.05 pH unit with a Beckman Model G pH meter calibrated with standard buffer solution.

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* Taken in part from the thesis submitted by BARBARA A. COONEY in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at Duke University, June, 1959.

Sample solutions were prepared at pH 5.53 with acetic acid–sodium acetate buffer. The sample solutions consisted of 0.1 M potassium chloride, 0.2 M buffer, and gelatin. For dye concentrations of $1 \cdot 10^{-3}$ M and less, 0.008% gelatin was sufficient as maxima suppressor, but 0.018% gelatin was necessary for $5 \cdot 10^{-3}$ M dye. The prepared sample solutions were allowed to stand for 10 to 12 h or were heated at 70° for 15 min to insure complete chelation. The solutions were deareated by bubbling purified nitrogen through them for 15 min. All measurements were carried out in a thermostat at 25 ± 0.01°.

Reagents

Superchrome Garnet Y was synthesized by coupling diazotized 2-aminophenol-4-sulfonic acid with resorcinol. The dye was purified by continuous extraction with ethanol. The dye was determined to be 82.8 ± 2.6% pure from a quantitative determination of azo nitrogen by reduction with standard titanium trichloride solution according to the method of KOLTOFF AND ROBINSON[8]. A stock solution of dye was prepared to be $1 \cdot 10^{-2}$ M with respect to available azo nitrogen.

The aluminum stock solutions were $1.007 \cdot 10^{-2}$ M prepared with 99.997% aluminum metal furnished by the Aluminum Company of America and $5.00 \cdot 10^{-3}$ M and $1.00 \cdot 10^{-2}$ M prepared with $AlK(SO_4)_2 \cdot 12H_2O$ (Mallinkrodt Chemical Works). The gallium stock solution was $4.99 \cdot 10^{-3}$ M prepared with gallium metal (Fisher Scientific Company) which was 99.5 ± 0.3% pure by analysis with 5,7-dibromo-8-hydroxyquinoline[9].

Calibration curves

Calibration curves of diffusion currents *versus* concentration of metal were prepared for each metal ion using a constant amount of dye and varying concentrations of metal. The diffusion current of the resulting polarographic waves for a given metal–dye system were linear functions of the metal ion present if sufficient dye were present to insure complete chelation. Calibration curves were prepared for aluminum and for gallium determinations using $1 \cdot 10^{-4}$ M SGY, $5 \cdot 10^{-4}$ M SGY, $1 \cdot 10^{-3}$ M SGY, and $5 \cdot 10^{-3}$ M SGY. The lower limit of dye concentration was determined by inherent fluctuations in the recorder circuit and the upper limit, by the solubility of the dye. The half-wave potentials of the first two waves of the aluminum-dye and gallium-dye systems were approximately —0.34 and —0.54 V respectively, and the half-wave potential of the third wave from the gallium–dye system was approximately —1.05 V. The half-wave potentials vary slightly with the concentration of dye.

By means of these calibration curves, concentrations of aluminum from $4.0 \cdot 10^{-6}$ M through $1.6 \cdot 10^{-3}$ M and concentrations of gallium from $4.0 \cdot 10^{-6}$ M through $2.0 \cdot 10^{-3}$ M can be determined with an accuracy of 3 to 5% using the first chelate wave (—0.54 V). Gallium can be determined from the third wave in the concentration range of $8 \cdot 10^{-6}$ M to $1.4 \cdot 10^{-3}$ M with an average precision of 4%. Figs. 1 and 2 show typical calibration curves for aluminum and for gallium respectively.

The effect of diverse ions was studied using 50-ml samples containing 10 mg of each ion. Foreign ions which were found to seriously interfere with this method of determining aluminum and gallium at pH 5.53 are zinc, manganese(II), cerium(IV), iron(III), vanadium(IV), and nickel. Cadmium and lead interfere with the determination of aluminum but not with the determination of gallium. Ions which were not found to interfere with the determination of aluminum or of gallium at pH 5.53 are magnesium, calcium, potassium, sodium, cesium, phosphate, nitrate, sulfate, and acetate.

Simultaneous determination of aluminum and gallium

Sample solutions for polarographic measurement were prepared with mixtures of aluminum and gallium and sufficient dye to insure complete chelation. The resulting polarograms exhibited, in most instances, three polarographic waves. The first or most positive wave results from the reduction of unchelated SGY, the second wave results from the reduction of chelated SGY, and the third or most negative wave appears to result from the reduction of gallium in the gallium–SGY chelate.

The metal ion concentrations were determined by assuming that all of the aluminum and gallium in the solutions are present as the metal–SGY chelates, that the third wave resulting from the gallium–SGY system is independent of the presence of aluminum, that the second waves from the aluminum–SGY system and from the gallium–SGY system have the same half-wave potential, and that the diffusion current of the second wave when both metals are in solution is equal to the sum of the diffusion currents of the individual metal chelates. The sample solutions were polarographed and then the concentration of aluminum and of gallium was determined as follows:

1. The concentration of gallium corresponding to the measured diffusion current of the third wave was determined from the appropriate calibration curve.

2. The diffusion current of the second wave for that concentration of gallium was read from the calibation curve.

3. The concentration of aluminum was determined using the diffusion current of the second wave resulting from electrolysis of the mixture. The diffusion current resulting from the reduction of aluminum–SGY chelate was determined by subtracting the diffusion current of the first gallium–SGY chelate wave (as determined in 2) from the diffusion current of the wave which results from the reduction of both metal chelates. The aluminum concentration corresponding to this diffusion current was found from the appropriate calibration curve.

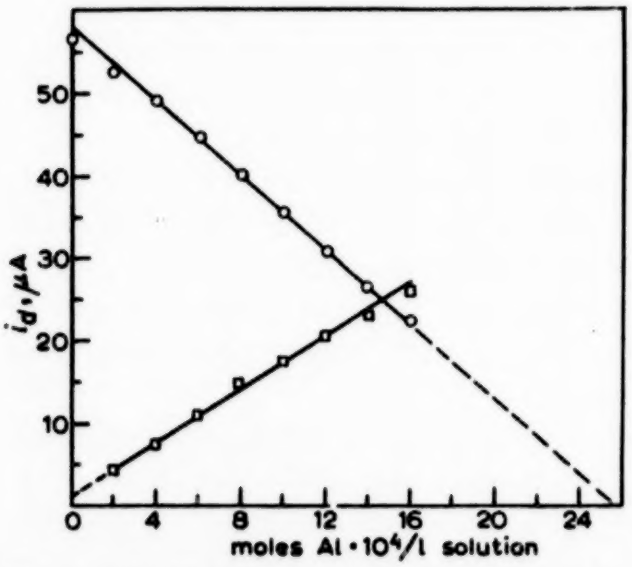

Fig. 1. Calibration curves for aluminum at pH 5.53 using $5 \cdot 10^{-3}$ *M* SGY.

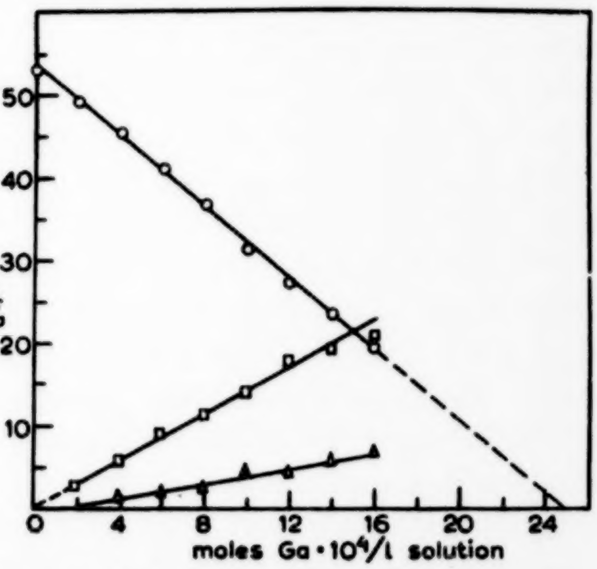

Fig. 2. Calibration curves for gallium at pH 5.53 using $5 \cdot 10^{-3}$ *M* SGY.

The results of analysis of mixtures of aluminum and gallium by this method are given in Table I. Aluminum was determined in all the mixtures with an average precision of ± 6.0%. Galllium was determined with an average precision of ± 7.8%, provided the aluminum concentration is less than five times that of the gallium. Aluminum, but not gallium, can be determined when the concentration of aluminum is more than five times that of gallium. This failure is caused in part by a small

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TABLE I

SIMULTANEOUS DETERMINATION OF ALUMINUM AND GALLIUM

Concn. SGY moles/l	*Aluminum (moles/l)*		*% error*	*Gallium (moles/l)*		*% error*
	Taken	*Found*		*Taken*	*Found*	
$1.00\cdot10^{-4}$	$1.00\cdot10^{-5}$	$1.07\cdot10^{-5}$	+ 7.0	$1.00\cdot10^{-5}$	$1.03\cdot10^{-5}$	+ 3.0
$1.00\cdot10^{-4}$	$3.00\cdot10^{-5}$	$2.83\cdot10^{-5}$	− 5.7	$1.00\cdot10^{-5}$	$0.93\cdot10^{-5}$	− 7.0
$5.00\cdot10^{-4}$	$5.00\cdot10^{-5}$	$5.20\cdot10^{-5}$	+ 4.0	$1.00\cdot10^{-5}$	$1.17\cdot10^{-5}$	+ 17.0
$5.00\cdot10^{-4}$	$1.00\cdot10^{-4}$	$1.10\cdot10^{-4}$	+ 10.0	$1.00\cdot10^{-5}$	no measurable wave	—
$1.00\cdot10^{-3}$	$1.00\cdot10^{-4}$	$0.96\cdot10^{-4}$	− 4.0	$1.00\cdot10^{-4}$	$1.05\cdot10^{-4}$	+ 5.0
$1.00\cdot10^{-3}$	$2.00\cdot10^{-4}$	$1.88\cdot10^{-4}$	− 6.0	$1.00\cdot10^{-4}$	$0.92\cdot10^{-4}$	− 8.0
$1.00\cdot10^{-3}$	$3.00\cdot10^{-4}$	$2.85\cdot10^{-4}$	− 5.0	$1.00\cdot10^{-4}$	$0.93\cdot10^{-4}$	− 7.0
$5.00\cdot10^{-3}$	$5.00\cdot10^{-4}$	$5.20\cdot10^{-4}$	+ 4.0	$1.00\cdot10^{-4}$	no wave	—
$1.00\cdot10^{-3}$	$2.00\cdot10^{-4}$	$1.85\cdot10^{-4}$	− 7.5	$2.00\cdot10^{-4}$	$2.13\cdot10^{-4}$	+ 6.5
$1.00\cdot10^{-3}$	$2.00\cdot10^{-4}$	$2.15\cdot10^{-4}$	+ 7.5	$3.00\cdot10^{-4}$	$2.75\cdot10^{-4}$	− 8.3

TABLE II

SEPARATION AND DETERMINATION OF ALUMINUM–GALLIUM MIXTURES

Mixture No.	*Aluminum (moles/l)*		*% error*	*Gallium (moles/l)*		*% error*
	Taken	*Found*		*Taken*	*Found*	
1	$5.00\cdot10^{-5}$	$5.00\cdot10^{-5}$	± 0	$1.00\cdot10^{-5}$	$1.00\cdot10^{-5}$	± 0
2	$1.00\cdot10^{-4}$	$1.08\cdot10^{-4}$	+ 8	$1.00\cdot10^{-5}$	$0.92\cdot10^{-5}$	− 8
3	$1.00\cdot10^{-4}$	$1.02\cdot10^{-4}$	+ 2	$1.00\cdot10^{-4}$	$1.05\cdot10^{-4}$	+ 5
4	$1.00\cdot10^{-4}$	$0.54\cdot10^{-4}$	− 46	$1.00\cdot10^{-3}$	$0.96\cdot10^{-3}$	− 4
5	$1.00\cdot10^{-3}$	$0.89\cdot10^{-3}$	− 11	$1.00\cdot10^{-5}$	$1.09\cdot10^{-5}$	+ 9
6	$1.00\cdot10^{-3}$	$0.48\cdot10^{-3}$	− 52	$1.00\cdot10^{-4}$	$1.10\cdot10^{-4}$	+ 10
7	$1.00\cdot10^{-3}$	$0.89\cdot10^{-3}$	− 11	$1.00\cdot10^{-3}$	$0.98\cdot10^{-3}$	− 2

anomalous wave appearing at —0.9 V in the aluminum–SGY system. This wave does not affect the diffusion currents of the two more positive waves, nor does it affect the third gallium wave directly. However, when the aluminum conc. is much greater than that of gallium, the diffusion current of the anomalous wave masks that of the third gallium wave. For the mixture of $5 \cdot 10^{-4}$ *M* aluminum and $1 \cdot 10^{-5}$ *M* gallium, the diffusion current of the third wave is too small for accurate measurement. This third wave failed to appear for $1 \cdot 10^{-4}$ *M* gallium in the presence of $5 \cdot 10^{-3}$ *M* SGY. (Fig. 2).

Separation and determination of mixtures of aluminum and gallium

Since the simultaneous determination of aluminum and gallium is limited to mixtures in which the ratio of aluminum to gallium does not exceed 5 to 1, a simple method of separating the cations before their polarographic determination was investigated. The method used, developed by SWIFT[10], depends upon the fact that gallium(III) chloride is soluble in diethyl ether while aluminum chloride is not. Mixtures of aluminum and gallium were prepared in 6 *N* hydrochloric acid. Volumes of 100 ml were extracted twice with 50 ml cold diethyl ether and twice with 40 ml ether. The ether portions were combined and extracted with 30 ml 3 *N* hydrochloric acid, which was prepared from purified hydrochloric acid. This final aqueous layer was combined with the other aqueous portion containing the aluminum. To the ether layers was added 5 ml distilled water and the ethereal and aqueous layers were evaporated almost to dryness. The respective residues were used in preparing the sample solutions to be polarographed. The concentrations of the metal ions were determined by means of the appropriate calibration curve. Typical results for such determinations are given in Table II.

The determination of gallium in these mixtures is satisfactory, but the determination of aluminum is poor. Further investigation of the procedure was made in an effort to improve the determination of aluminum, but without success.

Determination of aluminum and gallium in an aluminum alloy

The alloy used was from the National Bureau of Standards, Sample 85B, Aluminum Alloy (wrought), and contained 93.308% aluminum and 0.019% gallium. Other constituents of the alloy were copper, magnesium, manganese, iron, silicon, nickel, zinc, titanium, lead, and vanadium. All constituents except vanadium were present in larger quantity than gallium. Copper, iron, nickel, zinc, titanium, and lead were removed by reduction of a solution of the alloy at a mercury cathode at a potential of —1.1 to —1.2 V.

The alloy was first treated with 40 ml 1:1 hydrochloric acid and the remaining black residue was dissolved with 20 ml 6% hydrogen peroxide resulting in a clear, bright green solution. The solution was heated to remove excess hydrogen peroxide and was transferred to the electrolysis vessel. The solution was electrolyzed for 20-, 20-, 20-, 30-, and 30-min intervals at a stirred mercury cathode. The solution was then evaporated to 50 ml. An aliquot of this solution was used to prepare a sample solution which was approximately $1.4 \cdot 10^{-4}$ *M* aluminum. At this concentration of aluminum, the concentrations of interfering ions, including gallium, were negligible. The aluminum concentration was determined from the resulting polarogram and the appropriate calibration curve.

Another aliquot of the electrolyzed solution was extracted with cold diethyl ether as previously described. A sample solution was prepared for the polarographic determination of gallium from the residue of the combined ethereal layers. The concentration of gallium in the sample solution was of the order of 10^{-5} *M*.

The aluminum and gallium content of three samples of the alloy was determined by this method, and the results are given in Table III.

TABLE III

ALUMINUM AND GALLIUM DETERMINATIONS IN STANDARD ALLOY

Sample grams	*Aluminum*		*% Error*	*Gallium*		*% Error*
	mg taken	*mg found*		*mg taken*	*mg found*	
1.0025	935.4	979.0	+ 4.6	0.190	0.175	— 7.9
1.0053	938.0	904.5	— 3.6	0.191	0.208	+ 8.9
1.0042	937.0	898.0	— 4.2	0.191	0.205	+ 7.3
		Average	± 4.1		Average	± 8.0

Mixtures of aluminum, gallium, and indium

Preliminary investigations indicate that these metals can be determined over a limited concentration range from polarograms of the mixtures. A polarogram of the indium–SGY system shows two waves with essentially the same half-wave potentials as for the aluminum–SGY and gallium–SGY systems. However, a third wave appears at a half-wave potential of —0.64 V which is the half-wave potential of indium reduced in the absence of dye. In the presence of a three-fold excess of dye, the diffusion current of the third wave is a linear function of indium concentration.

Mixtures of aluminum, gallium, and indium can be determined if the unreacted SGY present exceeds the total metal ion concentration three-fold or more. The reduction of such a mixture of metal ions and SGY produces four polarographic waves. The gallium concentration is determined from the fourth (most negative) wave; the indium concentration from the third wave; and the aluminum concentration from the second wave after subtracting the contributions of the other two metal chelates from the total diffusion current.

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SUMMARY

Methods have been described for determining mixtures of aluminum and gallium when the ions are present in approximately the same concentration and when the concentration of aluminum exceeds the concentration of gallium by at least a factor of five. The average error of the determination of aluminum is ± 4 to 8% and that of gallium is ± 6 to 8%.

RÉSUMÉ

Une méthode est proposée pour le dosage polarographique de l'aluminium et du gallium, en présence l'un de l'autre. Erreur moyenne : ± 4 à 8% pour l'aluminium et ± 6 à 8% pour le gallium.

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ZUSAMMENFASSUNG

Es wird eine polarographische Methode beschrieben, mit welcher Aluminium und Gallium nebeneinander bestimmt werden können. Mittlerer Fehler für Aluminium: ± 4 bis 8%, für Gallium: ± 6 bis 8%.

REFERENCES

[1] J. W. Collat and L. B. Rogers, *Anal. Chem.*, 27 (1955) 961.
[2] H. H. Willard and J. A. Dean, *Anal. Chem.*, 22 (1950) 1264.
[3] M. Perkins and G. F. Reynolds, *Anal. Chim. Acta*, 18 (1958) 625.
[4] G. W. Latimer and C. D. Houston, *WADC Technical Report* 56-263, *ASTIA Document Nl.* AD97280 (1956).
[5] J. H. Saylor and C. R. Castor, *Anal. Chem.*, 24 (1952) 1369.
[6] L. H. Adcock, *M. A. Thesis*, Duke University (1953).
[7] B. A. Cooney, *M. A. Thesis*, Duke University (1956).
[8] I. M. Koltoff and C. Robinson, *Rec. trav. chim.*, 45 (1926) 169.
[9] E. Gastinger, *Z. anal. Chem.*, 126 (1944) 373.
[10] E. H. Swift, *J. Am. Chem. Soc.*, 46 (1924) 2375.

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EXTRACTION OF ZINC WITH TRI(ISO-OCTYL)AMINE IN METHYL ISOBUTYL KETONE AND COLORIMETRIC DETERMINATION WITH ZINCON IN THE ORGANIC PHASE*

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The aim of this investigation was to develop a colorimetric procedure for zinc after extraction from many interfering ions with an organic solution of a long chain aliphatic or aromatic amine. The effect of acid concentration in the aqueous phase and the time required for extraction were studied. The optimum conditions of basicity and time for the development of full, stable color were determined. The data thus obtained enabled a satisfactory colorimetric procedure for the determination of zinc *in situ* after extraction from aqueous solution to be established.

Mahlman, Leddicotte and Moore[1] found that methyldioctylamine and tribenzylamine are efficient extractants for zinc in hydrochloric acid solutions. The amines were dissolved in xylene, trichloroethylene and chloroform. Methyldioctylamine 8% (w/v) in trichloroethylene extracts zinc quantitatively from solutions containing hydrochloric acid above 3.0 *N*. Tribenzylamine 5% (w/v) in chloroform extracts less than threefourths of the zinc from solutions above 2.0 *N* in hydrochloric acid. Moore[2], in using 5% (w/v) tri(iso-octyl)amine in xylene and methyl isobutyl ketone for the extraction of uranium and plutonium, noted that zinc would be extracted also, along with other elements that form anionic chloride complexes.

Dithizone (diphenylthiocarbazone) extractions of heavy metals, including zinc, from a water phase into chloroform or carbon tetrachloride have become standard practice in the determination of such metals. However, dithizone is not selective and solutions of the reagent and its salts are very unstable. These characteristics of the reagent, along with the necessity of using very pure reagents and water, are disadvantages in dithizone determinations[3]. RUSH AND YOE[4] found that 2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene (Zincon) gave a dark blue precipitate (blue solution at high dilution) with zinc and developed a colorimetric method for zinc and copper in the presence of each other. An anion-exchange resin was used to separate zinc from a large number of common metal ions. The large amount of time required for such an ion-exchange separation is a disadvantage.

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* From the M. S. Thesis of Lucy E. Scroggie, University of Tennessee, March, 1959.

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APPARATUS AND REAGENTS

Spectrophotometer and colorimeter

Preliminary studies were done using a Beckman Model DU quartz spectrophotometer employing 1-cm, corex-glass, absorption cells. A Bausch and Lomb Spectronic 20 colorimeter with one-half inch (1.33 cm) cylindrical cells was used for subsequent work.

Zincon (2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene) solution

Zincon solutions were prepared by dissolving 0.130 g of finely powdered Zincon in 2 ml of 1 *N* sodium hydroxide and diluting to 100 ml with 95% ethanol. This gives a solution which is 0.002 *M*, based on a purity of 68% for the reagent. Zincon was obtained from LaMotte Chemical Products Co., Baltimore, Maryland. A fresh solution should be prepared weekly.

Standard zinc solutions

A standard zinc solution was prepared by dissolving 0.2500 g of reagent grade zinc metal in 1 ml of conc. hydrochloric acid and diluting to 250 ml with deionized water. This gives a solution containing 1000 μg of zinc per ml. A solution containing 100 μg of zinc per ml was prepared by diluting 10.0 ml of the stock solution to 100 ml with deionized water.

Tri(iso-octyl)amine-methyl isobutyl ketone

A solution containing 5% (w/v) tri(iso-octyl)amine in methyl isobutyl ketone was prepared. All organic solvents were practical grade and were used without further purification. All aqueous solutions were prepared from reagent grade chemicals and using deionized water which was prepared by passing ordinary distilled water through a bed of Amberlite MB-3 ion-exchange resin.

EXPERIMENTAL

Extraction of zinc from hydrochloric acid solutions with various amines in organic solvents

The percent of extraction of zinc from aqueous solutions of various hydrochloric acid concentrations with methyldioctylamine and tri(iso-octyl)amine in methyl

TABLE I

EXTRACTION OF ZINC WITH METHYLDIOCTYLAMINE AND TRI(ISO-OCTYL)AMINE IN METHYL ISOBUTYL KETONE AS A FUNCTION OF HYDROCHLORIC ACID CONCENTRATION

HCl, N	*% Zinc extracted with various extractants*	
	Methyldioctylamine[a]	*Tri(iso-octyl)amine*[b]
1.0	92.00	100.00
2.0	100.00	100.00
3.0	100.00	97·75
4.0	95·50	100.00
5.0	94·25	100.00

[a] 8% (w/v) methyldioctylamine in methyl isobutyl ketone.
[b] 5% (w/v) tri(iso-octyl)amine in methyl isobutyl ketone.

isobutyl ketone is shown in Table I. Solutions containing 100 μg of zinc in 5.0 ml of aqueous phase were shaken with 10.0 ml of the amine solution for 3 min at room temperature. The amount of zinc remaining in the aqueous phase after extraction was determined colorimetrically using the procedure developed by RUSH AND YOE[4].

Although both methyldioctylamine and tri(iso-octyl)amine extract zinc quantitatively from hydrochloric acid solutions, a 5% (w/v) solution of the latter amine in methyl isobutyl ketone was chosen for all subsequent study, since it is less expensive and obtained more easily. Non-equilibrated organic phases were used in all extractions. A 2.0 *N* concentration of hydrochloric acid gave sufficient acid to form the extractable anionic zinc complex and to obtain efficient extraction even though acid is extracted by the tertiary amine-organic solvent phase.

The extraction of zinc as a function of extraction time at 25° is shown in Table II. The amount of zinc remaining in the aqueous phase after extraction was determined colorimetrically as before.

While the extraction of zinc is shown in Table II to be quantitative after 1 min of shaking, it was found later that 3 min were required to remove all of the zinc from a solution containing large quantities of magnesium.

TABLE II

EXTRACTION OF ZINC FROM 2.0 *N* HYDROCHLORIC ACID WITH 5% TRI(ISO-OCTYL)AMINE–METHYL ISOBUTYL KETONE AS A FUNCTION OF EXTRACTION TIME

Extraction time (min)	*Zinc extracted (%)*
0.5	98.75
1.0	100.00
2.0	100.00
3.0	100.00

Extraction and colorimetric determination of zinc in situ

Attempts were made to correlate the determination of zinc in the organic phase with Zincon reagent to the determination in the aqueous phase. The reagents and the ketone phase from the extraction step were made to form a single phase by dilution with 95% ethanol. A homogeneous solution was observed, but inconsistent absorbancies were noted for replicate determinations on solutions containing known zinc concentrations. The difficulties seemed to lie in the buffer solution used. In order to

TABLE III

ABSORBANCY AS A FUNCTION OF THE POTASSIUM HYDROXIDE CONCENTRATION[a]

KOH, N	*Absorbancy*		
0.10	0.568	0.570	0.570
0.20	0.277	0.277	0.274
0.30	0.139	0.128	0.131
0.40	0.073	0.068	0.080
0.50	0.053	0.046	0.066

[a] Absorbancies of solutions containing 2 μg of zinc per ml measured at 620 mμ against a reagent blank.

surmount these difficulties, various volumes of 5.0 *N* potassium hydroxide were added to the ketone layer containing the zinc with no attempt to buffer the solutions. The effect of the potassium hydroxide concentration in the final 50-ml volume on the absorbancy of a series of solutions containing the same amount of zinc is shown in Table III. Solutions whose final concentration were 0.10 *N* in potassium hydroxide gave the maximum absorbancies. For this reason and because solutions treated in this manner gave reproducible values of absorbancy, this concentration of potassium hydroxide was adopted in the final procedure.

In order to determine the length of time required for full color development and the stability of the color, a time study was carried out: Table IV. The time was measured in min after mixing and the absorbancy was measured at 620 mμ against a reagent blank. The absorbancy of the blank became constant immediately, but full color development required 8 min. The absorbancy increased only 2% after standing for 24 h.

TABLE IV

ABSORBANCY AS A FUNCTION OF TIME AFTER MIXING[a]

Time (min)	*Absorbancy*	*Time (min)*	*Absorbancy*
1.0	0.250	14.0	0.560
2.0	0.368	16.0	0.560
3.0	0.455	18.0	0.560
4.0	0.510	20.0	0.560
5.0	0.539	25.0	0.560
6.0	0.545	30.0	0.560
7.0	0.555	35.0	0.560
8.0	0.560	40.0	0.560
9.0	0.560	45.0	0.560
10.0	0.560	50.0	0.560
11.0	0.560	55.0	0.560
12.0	0.560	60.0	0.560

[a] Absorbancy of a solution containing 100 μg of zinc measured at 620 mμ against a reagent blank.

RECOMMENDED PROCEDURES

Calibration curve

To suitable aliquot portions of a standard zinc solution, add 1.0 ml of 10 *N* hydrochloric acid and enough water to give a total volume of 5.0 ml. Shake with 10.0 ml of 5% (w/v) tri(iso-octyl)amine–methyl isobutyl ketone in a 30-ml separatory funnel for 3 min. Remove and discard the aqueous phase. Dry the stem of the funnel with a strip of filter paper. Drain the ketone layer into a 50-ml volumetric flask. Add 5.0 ml of 1.0 *N* potassium hydroxide, 5.0 ml of methyl isobutyl ketone, and 3.0 ml of Zincon solution. Dilute to the mark with 95% ethanol and mix thoroughly. After 8 min standing, measure the absorbancy at 620 mμ against a reagent blank. Plot absorbancies against concentration expressed as μg of zinc per ml.

Procedure for magnesium-base alloys

Dissolve a suitable size sample in dilute hydrochloric acid and dilute to a known volume. Transfer a suitable aliquot portion to a 30-ml separatory funnel. Add 1.0 ml of 10 *N* hydrochloric acid and enough water to give a total volume of 5.0 ml. Extract, develop the color, and measure as described under *calibration curve*. Determine the zinc concentration from a calibration curve.

Procedure for aluminum-base alloys

To the sample add 3 ml of 19 *N* sodium hydroxide. After 3 min, add 3 ml of water. After the reaction subsides, heat the solution to boiling and boil for 3 min. Cool to room temperature and acidify with hydrochloric acid. Transfer the solution to a volumetric flask and dilute to a known volume. Transfer a 4.0-ml aliquot to a 30-ml separatory funnel and add 1.0 ml of 10 *N* hydrochloric acid. Shake for 2 min with 10.0 ml of 5% (w/v) tri(iso-octyl)amine–methyl isobutyl ketone. Remove and discard the aqueous phase. Wash the ketone layer with a fresh 5.0-ml portion of 2.0 *N* hydrochloric acid and discard the aqueous phase. Back-extract the zinc by shaking the ketone layer for 1 min with two 5.0-ml portions of 0.05 *N* hydrochloric acid. Combine the aqueous phases and transfer a 4.0-ml aliquot to a clean 30-ml separatory funnel. Add 1.0 ml of 10 *N* hydrochloric acid. Extract for 2 min with 10.0 ml of 5% (w/v) tri(iso-octyl)amine–methyl isobutyl ketone. Remove and discard the aqueous phase. Dry the stem of the funnel with a strip of filter paper. Transfer the ketone layer to a 50-ml volumetric flask. Proceed with the color development and measurement as described under *calibration curve*. Determine the zinc concentration from a calibration curve.

DISCUSSION

Nature of the extraction

Zinc is extracted by tri(iso-octyl)amine–methyl isobutyl ketone as the chloroanionic complexes trichlorozincate(II) or tetrachlorozincate(II). The extraction probably proceeds through hydrogen-bonding and ion association between the negatively-charged $ZnCl_3^-$ or $ZnCl_4^{-2}$ and the tri(iso-octyl)ammonium ion or the solvonium ion of the ketone.

Chromogenic system

The potassium hydroxide necessary to give full color development probably slowly converts the extracted ion association complex to the zinc(II) ion, which then reacts with the Zincon.

The actual pH of the solutions at the time of color development was not ascertained. The potassium hydroxide concentration for best results is given as 0.1 *N*, but of necessity the actual concentration is less than this, since some of the hydroxide reacts with co-extracted acid.

Following AYRES' treatment[5], the concentration range of best accuracy extends from 0.6 to 3.0 μg of zinc per ml when using the 1.33-cm cylindrical cells supplied with the colorimeter. This corresponds to from 30 to 150 μg of zinc in the initial 5.0 ml sample volume. Two solutions containing 0.02 μg of zinc per ml gave an average absorbancy of 0.005 unit, which gives about 0.004 μg per ml as the minimum detection limit. The method gives 3.39% relative analysis error per 1% absolute photometric error. The molar absorbancy index, calculated on the basis of the molarity of the zinc solution, is 14,000 at 620 mμ.

The blank value is rather large (usually about 0.14 absorbancy unit) because the reagent absorbs to some extent at 620 mμ and because exhaustive purifications of the reagents were not attempted. An absorbancy *versus* wavelength curve, similar to the curve given by RUSH AND YOE[4], was obtained for solutions analyzed by the recommended procedure.

Effect of diverse ions

The effect of added diverse ions on the analysis of zinc solutions by the recommended procedure is shown in Table V. Copper(II) is by far the most serious interferent.

TABLE V

EFFECT OF DIVERSE IONS ON THE ANALYSIS OF ZINC SOLUTIONS[a]

Element	*Amount present (μg total)*	*Zinc recovered (%)*	*Tolerance limit (μg total)*
Al(III)	10,000	109	1,100
Cd(II)	1,000[b]		
Cr(III)	10,000	57	230
Cr(VI)	1,000	102	500
Co(II)	3,800[c]		
Cu(II)	250	199	
	100	134	<10
Fe(II)	500	84	30
Fe(III)	1,000	74	40
Pb(II)	2,000	102	1,000
Mn(II)	10,000	102	5,000
Mo(VI)	1,000	100	>1,000
Ni(II)	10,000	88	830
Sn(IV)	1,000	108	120
V(V)	1,000	115	70

[a] Each solution contained 100 μg of zinc.
[b] Solutions containing Cd(II) gave insoluble precipitates.
[c] Solutions containing Co(II) were cloudy.

TABLE VI

ZINC ANALYSES ON NATIONAL BUREAU OF STANDARDS ALLOYS

Sample	*Zinc value, %*			
	Certified	*Found*		
Magnesium-base alloy 171	1.05 ± 0.01[a]	1.00	1.06	
		1.04	0.98	
		1.02	1.06	
		Average		1.03
		S. D.		0.03
Aluminum-base alloy 87	0.077 ± 0.007[a]	0.075	0.078	
		0.075	0.080	
		0.072	0.076	
		Average		0.076
		S. D.		0.003

[a] Values given are mean of certificate values, with associated standard deviation.

The interference of copper and of many other ions can be removed, or at least minimized, by the back-extraction of zinc into 0.05 N hydrochloric acid and re-extraction. Cadmium(II) and cobalt(II) tend to give precipitates in the final solutions, indicating that these ions are also extracted, but that they are insoluble at the final pH. Many interferences can be removed by prior extractions. For instance, chromium(VI) is completely extracted from solutions 1 N in hydrochloric acid with methyl isobutyl ketone[6,7], and iron (III) from solutions 5.0 N in hydrochloric acid with methyl isobutyl ketone[8] or from solutions 8.0 N in hydrochloric acid with isopropyl ether[1].

Analysis of National Bureau of Standards Alloys

Analysis of two National Bureau of Standards samples of magnesium- and aluminum-base alloys was carried out using a Bausch and Lomb Spectronic 20 colorimeter with one-half inch (1.33 cm) cylindrical cells. The results of the analyses are given in Table VI.

SUMMARY

A study was made of the extraction of zinc from hydrochloric acid solutions with solutions of methyldioctylamine and tri(iso-octyl)amine in methyl isobutyl ketone. Quantitative extraction was accomplished from 2 N hydrochloric acid with 5% (w/v) tri(iso-octyl)amine–methyl isobutyl ketone. A procedure was developed for the colorimetric determination of zinc in the organic phase after extraction using 2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene (Zincon).

RÉSUMÉ

Une étude a été effectuée sur l'extraction du zinc, en solution chlorhydrique, au moyen de solutions de méthyldioctylamine et de tri(iso-octyl)amine dans la méthylisobutylcétone. Une méthode est proposée pour le dosage colorimétrique du zinc au moyen de zincon(carboxy-2-hydroxy-2′-sulfo-5′-formazylbenzène).

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Extraktion von Zink aus salzsaurer Lösung mit Hilfe von Methyl-dioctylamin oder Tri-(iso-octyl)-amin in Metylisobutylketon. Die quantitative Bestimmung des Zinks im organischen Lösungsmittel erfolgt colorimetrisch mit Zincon (2-Carboxy-2′-hydroxy-5′-sulfo-formazyl-benzol).

REFERENCES

[1] H. A. Mahlman, G. W. Leddicotte and F. L. Moore, *Anal. Chem.*, 30 (1958) 1939.
[2] F. L. Moore, *Anal. Chem.*, 30 (1958) 908.
[3] E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 2nd Ed., Interscience Publishers, New York 1950.
[4] R. M. Rush and J. H. Yoe, *Anal. Chem.*, 26 (1954) 1345.
[5] G. H. Ayres, *Anal. Chem.*, 21 (1949) 652.
[6] A. E. Weinhardt and A. N. Hixson, *Ind. Eng. Chem.*, 43 (1951) 1676.
[7] H. A. Bryan and J. A. Dean, *Anal. Chem.*, 29 (1957) 1289.
[8] H. Specker and W. Doll, *Z. anal. Chem.*, 152 (1956) 178.

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THE DETERMINATION OF NITROGEN IN METALS BY ISOTOPE DILUTION*

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INTRODUCTION

Isotope dilution procedures have been developed for the determination of oxygen in some metals by KIRSHENBAUM, *et al.*[1-4] The technique was also extended to the determination of carbon in steels and related metals by HICKAM[5]. In general, the basis of these procedures is one of vacuum heating or vacuum fusion of the samples along with a 'master alloy' containing the enriched isotopic tracer. KIRSHENBAUM, HINDIN and GROSSE used the isotope dilution technique to determine the nitrogen content of organic compounds[6], the method developed involving principles employed in the classical Dumas determination. Generally speaking, the procedures described by these authors have not been applied to sample material that contained very small amounts of the impurity being determined in spite of the fact that in principal the technique should be amenable to such assays.

Despite these applications of the general techniques to the assay of the above non-metallic elements, no similar approach has been applied to the problem of assaying metals for their nitrogen content, especially in the very low concentration range. An attempt in these laboratories several years ago to develop a 'master alloy'-vacuum fusion procedure for nitrogen determinations failed to give satisfactory results. In a general sense, this procedure is not simple nor is it very convenient. Furthermore, the time required to do an analysis is long and one has all the problems associated with the vacuum fusion procedure. In spite of the simplicity of the Dumas procedure which makes it an enticing one, it is not applicable to metal systems.

Two principal methods are used to determine nitrogen in metals, the vacuum fusion method and the Kjeldahl method. Many different variations of the general procedures are used primarily involving the final handling of the evolved nitrogen gas. In vacuum fusion procedures, if the only gas evolved is nitrogen, a simple volumetric measurement is sufficient to obtain the desired result[7]. When gas mixtures are evolved, some analytical procedure must also be employed which will give proper results with small amounts of gas sample. Mass spectrometric methods have been used for such analyses[8]. In the Kjeldahl method, after the samples have been dissolved and the ammonia separated from the solution, some appropriate titration procedure[9] or photometric method is generally applied[10].

The isotope dilution method for nitrogen described in this paper was developed in order to determine trace amounts of nitrogen in metals more conveniently than by vacuum fusion and more accurately and precisely than by the Kjeldahl method. In principle, the method consists of adding a known amount of ammonium sulfate of known ^{15}N content, which is different from normal, to a weighed amount of metal, dissolving the metal in some appropriate acid and determining the final amount of ^{15}N in the resultant mixture. The amount of nitrogen in the metal can be calculated from this information. Except for the isotope determination with the mass spectrometer, all of the operations involved in handling the samples are classical ones for which chemists have a long standing tradition. Quantitative manipulation of small amounts of gas under high vacuum conditions are unnecessary.

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* Contribution No. 719. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

EXPERIMENTAL PROCEDURE

Five to seven grams of the metal sample are weighed to one-tenth of a mg. At least three tenths of a mequiv. of tracer ammonium ion is added from a weight buret. The sample is then dissolved in as little acid as possible, using conventional dissolution procedures where they apply to the various metals. The solution is transferred to a Kjeldahl flask, made alkaline and distilled for 3 min into 10 ml of 0.1 *N* hydrochloric acid. The NH_4^+ in the distillate is then oxidized to N_2 by alkaline sodium hypobromite in an appropriate gas generating and collecting apparatus[11]. The gas is then introduced into a dual-collector, isotope-ratio mass spectrometer and assayed for ^{15}N by determining the $29^+/28^+$ ion current ratio. The $^{40}A^+$ ion peak in the sample gas is monitored to check for contamination due to air, in which case proper corrections are applied[12].

CALCULATIONS

The general equation used to calculate the percent nitrogen in the metal sample is:

$$\%\ \text{N} = \frac{(14.008)\ (\text{mequiv. tracer NH}_4^+)}{\text{mg of sample}} \times \frac{\text{at. \% tracer } ^{15}\text{N} - \text{at. \% mixture } ^{15}\text{N}}{\text{at. \% mixture } ^{15}\text{N} - \text{at. \% sample } ^{15}\text{N}} \times 100 \tag{1}$$

where a value of 0.3649 is used for the "at. % sample ^{15}N". The "at. % ^{15}N" in the sample gas is calculated by using the formula:

$$\text{at. \% } ^{15}\text{N} = \frac{R}{2 + R} \times 100 \quad \ldots\ldots\ldots\ldots \tag{2}$$

where R is the $29^+/28^+$ ion current ratio obtained from the mass spectrometer. This ratio is corrected for air leaks if necessary, and for the background of the mass spectrometer and then normalized by comparing with a standard nitrogen tank sample whose absolute isotopic abundances have been previously determined[13].

RESULTS

A variety of metals were obtained from the Ames Laboratory of the U. S. Atomic Energy Commission and from several commercial producers. Where previous analyses were available, comparisons were made between this procedure and ones previously employed. Unfortunately, no information regarding the precision of most of the independent analyses was available. However, the precision of the results of the present study are reported here as an indication of what might be expected from the isotope dilution procedure. Tables I and II contain summaries of the results obtained on a variety of metals and alloys. In all cases cited, hydrochloric acid was the principal reagent used to dissolve the sample. Variations involving the addition of other reagents were applied in appropriate cases. The determinations of the nitrogen content in reagent grade conc. hydrochloric acid is also reported in Table I.

TABLE I

DETERMINATION OF THE NITROGEN CONTENT OF NON-FERROUS METALS AND ALLOYS

Metal sample	*Previous analysis in p.p.m. nitrogen*[a]	*Isotope dilution in p.p.m. nitrogen*	*No. of determs.*[b]	*Deviation* ± %
Thorium[c]	100	57	8	3
Lanthanum 1[c]	—	271	5	5
Lanthanum 2[c]	—	154	5	8
Yttrium XC-123t[c]	385	164	3	8
Yttrium XC-123b[c]	332	248	5	6
Yttrium XC-120b[c]	138	87	6	9
Yttrium XC-128b[c]	87	114	3	5
Yttrium XC-129t[c]	55	88	3	4
Yttrium XC-119b[c]	107	95	4	9
Yttrium C-174-B-t[c]	214	254	3	2
Nichrome, heat 7444[d]	265 ± 15 (Kjeldahl) 237 ± 44 (Vac. fusion)	387	3	0.5
Ferrotitanium, 70% Ti[e]	1300	1366	4	2
Ferrotitanium, 30% Ti[e]	210	150	4	12
Ferromanganese, med C[e]	460	497	4	2
Manganese, electrolytic, nitrided, 94% Mn[e]	5.16%	5.69%	4	1
Ferrochrome, low C, 71% Cr[e]	770	848	4	12
Chromium, low C, 97.5% Cr[e]	370	408	4	6
Chromium, electrolytic, 97.5% Cr[e]	50	29	4	6
Titanium 99.8% Ti[e]	60	77	1	—
Aluminum 40[e]				
Vanadium 60[e]	350	353	3	6
Vanadium (crystal bar) CO-2-108[c]	150	194	3	4
Concentrated hydrochloric acid[f]	3	2.4	2	6

[a] Analytical results obtained from source of samples.

[b] Each determination represents a separate portion of the sample treated individually. No aliquots of solutions were taken.

[c] Ames Laboratory of the U. S. Atomic Energy Commission, Ames, Iowa.

[d] The Driver-Harris Co., Harrison, New Jersey.

[e] Electrometallurgical Co., Niagara Falls, New York.

[f] E. I. Dupont de Nemours & Co., Wilmington, Delaware.

TABLE II

DETERMINATION OF THE NITROGEN CONTENT OF FERROUS METALS AND ALLOYS

Metal sample	*Previous analysis in p.p.m. nitrogen*[a]	*Isotope dilution in p.p.m. nitrogen*	*No. of determs.*[b]	*Deviation* ± %
Steel A9 [c]	2400	2415	3	2
Steel 84 [c]	200	180	2	12
Steel A2a [c]	7500	7469	10	0.5
Cast Iron 8h [d]	170	191	2	5
Steel 1-335 [e]	8 (v.f.)	2	3	3
Steel 1020 [e]	24 (v.f.)	48	3	0.6
Steel E [e]	4 (v.f.)	52	2	5
Steel RH1081 [e]	20 (v.f.)	40	3	5
Steel 1296-1 [e]	50 (v.f.)	42	3	7
Steel RH836 [e]	34 (v.f.)	61	3	2
Steel 154082 [e]	64 (v.f.)	72	2	3
Steel 84997 [e]	172	172	3	1
Steel 92171 [e]	226	247	3	1
Steel J-3245 [f]	4 (v.f.)	35	3	9
Steel J-3049 [f]	4 (v.f.)	29	3	3
Steel K-4115-2 [f]	430	427	3	1.2
Steel K-4116-1 [f]	70 (v.f.)	71	3	9.4
Steel K-4320-1 [f]	140	107	4	7.4
Steel K-4323-1 [f]	3900	3996	3	1.8
Steel K-4329-1 [f]	2200	2277	3	0.6
Steel K-4331-1 [f]	1600	1749	3	2
Steel K-4332-1 f	2100	2201	3	1.5
Steel K-4335-1 [f]	70 (v.f.)	79	3	1.4
Iron, electrolytic [g]	—	31	3	6
Iron, electrolytic, fired in moist H_2 [g]	—	22	3	2

v.f. = vacuum fusion.

[a] Analytical results obtained from supplier of samples.

[b] Each determination represents a separate portion of the sample treated individually. No aliquots of solutions were taken.

[c] Ford Motor Co. Research Laboratory, Dearborn, Michigan.

[d] National Bureau of Standar, Washington, D. C.

[e] Jones and Laughlin Steel Corp., Pittsburg, Pa.

[f] U.S. Steel Corp., Pittsburgh, Pa.

[g] The G. Fredrich Smith Chemical Co., Columbus, Ohio.

DISCUSSION OF FACTORS AFFECTING RESULTS

In a strict sense, any variation in the isotopic abundance of an impurity in a material, compared with the isotopic abundance in the principal source of the impurity may introduce errors into an analytical procedure based on isotope dilution. In the case of a nitrogen impurity in metals, the principal source of contamination is the atmosphere or chemicals used in nitriding operations. Thus the isotopic abundance of ^{15}N in the metals should be expected to be that of the atmosphere or not very far from it. Examination of equation (1) indicates that if the ^{15}N content of the tracer is at least ten-fold enriched over that of the atmosphere, then under the ordinary conditions of this procedure, variation of as much as ± 3% in the isotope abundance of nitrogen from the metal samples will not introduce an error greater than ± 0.4% in the final result. As a check on what variations may reasonably be expected in representative materials, the ^{15}N abundance was measured in reagent grade ammonium sulphate and in the hydrolysates of a Mg_3N_2-MgO mixture made by burning Mg in air, of thorium nitride in the presence of a large excess of thorium metal and in titanium nitride. These nitrides were prepared by the reaction of air, nitrogen or ammonia with the metal involved. The absolute ^{15}N abundance for these materials was found to vary from 0.365 to 0.375 at. %; therefore, any error introduced into the determination from this source is negligible compared to other possible sources of errors.

The method described in this paper depends upon the conversion to NH_4^+ of all the nitrogen held as an impurity in a metal when the metal is dissolved in an acid. In discussions with several metallurgists*, the possible existence of free nitrogen in certain nitrided steels which were austenitic in character was cited. Also, the possibility of nitrogen–carbon combinations in metals of high carbon and nitrogen content was given. If the former is true, then N_2 gas might be liberated among the other gases when these metals are dissolved. In the latter case, hydrogen cyanide, complexed CN^- or amines formed as hydrolysis products might be expected to be present either in the evolved gases or in the solution.

A high nitrogen, austenitic type steel (A2a, Table II) was dissolved in hydrochloric acid and all the evolved gas collected. No free N_2 was detected in this gas by mass spectrometric methods. The gas from the same sample was passed through a solution of sodium hydroxide which was subsequently analysed for the presence of CN^-. No cyanide was detected in the alkali solution nor was any complexed cyanide found in the acid solution containing dissolved iron. Attempts to detect simple amines in gases evolved when solutions of this steel were made alkaline, failed. However, because the mass spectrometer is not too sensitive to these substances other corroborating experiments were performed. Dissolving this steel in H_2SO_4 followed by fuming to SO_3 in the conventional Kjeldahl manner resulted in nitrogen assays that were identical with those made when other acid solvents were used. Thus the presence of simple amines as products of reaction in materials similar to this particular steel is unlikely. Repetition of these experiments on other metal samples gave identical results. The weight of the evidence is that only NH_4^+ is produced when nitrogen-containing metals are dissolved in acids. On the basis of this evidence the isotope dilution method for assaying the nitrogen content of metals and alloys appears to be sound and reliable.

The Kjeldahl-type distillation indicated in the experimental procedure is not necessary but has many advantages. Because of the design of the apparatus employed, a small volume of solution was needed to oxidize the NH_4^+ solution to N_2 gas. Concentration of ammonia by distillation resulted in considerable time saving. It also served as a convenient means of reducing the amount of acid because the evolved ammonia was caught in 10 ml of 0.1 *N* hydrochloric acid. This greatly simplified the alkaline hypobromite oxidations. Separation of the ammonia from certain heavy metal ions also aided the oxidation step inasmuch as their presence causes undesirable side reactions, notably the production of gaseous O_2 which interferes with the mass spectrometry by decreasing instrument stability.

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* Private Communication, members of Ames Laboratory Nuclear Metallurgy School, July 1–August 24, 1957, Iowa State College Ames, Iowa.

A ten-fold enriched ^{15}N tracer in the form of an ammonium sulfate solution was used in most of the work reported here. This was assayed by careful Kjeldahl titrations employing electrometric methods to determine the end-points. As a check, the solutions were also assayed by an isotope dilution method using as the standard, recrystallized, reagent-grade ammonium sulphate which had been compared with atmospheric nitrogen for its isotope abundance. Weighed amounts of vacuum dried crystals were mixed with a weighed amount of the tracer solution. Excellent agreement with the titrations were obtained in this manner.

Although tracers either enriched or depleted in ^{15}N were used during the course of the work, the enriched tracer gave more consistent and precise results. This was primarily because of the limit placed on any depleted material due to the small amount of ^{15}N existing in natural sources. The absolute abundance of ^{15}N in atmospheric nitrogen is 0.3649 at. % which gives a 29/28 ratio of 0.007325. Ratio measurements considerably below this figure are difficult to make with great precision. On the other hand, employing a ten-fold enriched tracer gives a value for this ratio of about 0.073250 which can be easily measured to four significant figures thereby allowing for considerable improvement in the overall precision for the nitrogen analyses. It should be pointed out that when more highly concentrated tracers are employed a point of diminishing returns is reached because of the effect of the 30^+ ion current on the ^{15}N assays. For an approximately ten-fold enriched tracer, only the $29^+/28^+$ ratio must be measured. At greater ^{15}N concentrations the 30^+ ion current must also be measured, adding to the time consumed in making the measurement without contributing greater precision.

Ideally, half of the nitrogen in the mixture should come from the metal sample and half from the tracer. For a low-nitrogen impurity this would necessitate a prohibitively large sample. Using a ten-fold enriched tracer, very good precision was obtained when a nitrogen ratio of one part from the sample to fifteen parts from the tracer was attained. For less favorable dilutions, only the precision of the analysis suffered, since it was still possible to get an estimate of the N present. More precise results were then obtainable if warranted, by adjustment of the amount of sample taken.

In the outlined procedure, it was stated that three-tenths of a mequiv. of tracer ammonium ion was always added. This produced the minimum amount of nitrogen gas needed to give enough pressure in the sample system of the mass spectrometer used in the work. Thus the operator was always assured of enough gas to assay in the instrument. Some variation is reported here between results obtained by this method and those obtained by others. No reasons for these are apparent. It is the feeling of the authors that some of the questions involving the fate of nitrogen when metal samples are dissolved in acids has been clarified. No claim is made that exceptions to our findings cannot exist but the large variety of sample materials chosen and tested justifies confidence in the reported results. The discrepancy between these data and some of the samples previously analysed by the vacuum fusion technique is not surprising inasmuch as similar findings have been observed by a great number of workers.

With a few slight changes in the experimental procedure, the isotope dilution method as described here can be applied to many different types of nitrogen analyses in inorganic and organic compounds.

References p. 295

ACKNOWLEDGEMENTS

The authors wish to acknowledge the fine cooperation of all the commercial laboratories listed in Tables I and II that supplied metal and alloy samples which had previously been analysed for nitrogen. The analytical group of the Ames Laboratory also deserves special mention.

SUMMARY

A wet chemical procedure for determining the amount of nitrogen in a metal or alloy has been developed which utilizes the isotope dilution technique. Ammonium sulfate, either enriched or depleted in ^{15}N, is added to the metal sample during solution procedures. Ammonium ions resulting from the hydrolysis of bound nitrogen in the metals mix with that of the tracer and the total is then oxidized to N_2 in which form the element is analyzed in the mass spectrometer. The method has been tested on a variety of metals and alloys including thorium, lanthanum, yttrium, titanium, chromium, manganese, various steels, nickel-chromium, ferrotitanium, ferromanganese and ferrochromium. The range of nitrogen in these materials was from 2 ppm to almost 6%. Average precision was generally better than ± 5%.

RÉSUMÉ

Une méthode par dilution isotopique est proposée pour le dosage de l'azote dans un métal ou dans un alliage. On ajoute à l'échantillon à analyser du sulfate d'ammonium avec une teneur en ^{15}N connue (et différente de la normale). Le total des ions ammonium (ceux qui ont été additionnés et ceux provenant de l'azote à doser) est oxydé en N_2, que l'on analyse au spectromètre de masse.

ZUSAMMENFASSUNG

Es wird ein Verfahren beschrieben zur Bestimmung von Stickstoff in Metallen und Legierungen durch Anwendung der Isotopen-Verdünnungsmethode. Zur Analysenprobe wird eine gemessene Menge Ammoniumsulfat mit bekanntem N^{15} Gehalt gegeben. Die Gesamtmenge der Ammonium-Ionen wird zu Stickstoff oxydiert und dieser im Massenspektrometer analysiert.

REFERENCES

[1] A. D. KIRSHENBAUM AND A. V. GROSSE, *Anal. Chim. Acta*, 16 (1957) 225.
[2] A. D. KIRSHENBAUM, R. A. MOSSMAN AND A. V. GROSSE, *Trans. Am. Soc. Metals*, 46 (1954) 525.
[3] A. D. KIRSHENBAUM AND A. V. GROSSE, *Trans. Am. Soc. Metals*, 45 (1953) 758.
[4] A. D. KIRSHENBAUM, *Anal. Chem.*, 29 (1957) 980.
[5] W. M. HICKAM, private communication.
[6] A. D. KIRSHENBAUM, S. G. HINDIN AND A. V. GROSSE, *Nature*, 160 (1947) 187.
[7] W. J. MCMAHON AND L. S. FOSTER, *J. Chem. Educ.*, 30 (1953) 609.
[8] D. T. PETERSON AND D. J. BEERNTSEN, *Anal. Chem.*, 29 (1957) 254.
[9] H. F. BEEGHLY, *Anal. Chem.*, 24 (1952) 199.
[10] J. A. CORBETT, *Metallurgia*, 49 (1954) 206.
[11] D. RITTENBERG, A. S. KESPON, F. ROSEBURY AND R. SCHOENHEIMER, *J. Biol. Chem.*, 127 (1939) 291.
[12] P. F. HOLT AND B. P. HUGES, *J. Chem. Soc.*, (1955) 95.
[13] G. JUNK AND H. J. SVEC, *Geochim. et Cosmochim. Acta*, 14 (1958) 234.

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Short Communications

Separation and micro determination of formaldehyde and methanol in excess azoalkanes, methylal and lower esters

Formaldehyde and methanol are major products in the gas phase photo-oxidation of methyl radicals. In kinetic work, with azomethane as a source of methyl radicals, the problem was to analyse both substances quantitatively in a 300-fold excess of azomethane.

All the methods described in the literature lead, in the aqueous phase, to hydrolysis of the azomethane producing formaldehyde and methyl hydrazine[1] and cannot therefore be used. It was found that the azomethane could be separated from the formaldehyde and methanol simply by blowing nitrogen through an aqueous solution of the mixture. Azomethane is removed quantitatively whereas formaldehyde and methanol are kept back.

The procedure described has been applied also to the separation of a few other substances which are of some interest to the gas kineticist and was successful in the case of azoethane, methylal, and esters like methyl formate.

A sample containing not more than 120 μg formaldehyde and 450 μg methanol in the presence of excess azomethane is dissolved in 2 ml water and placed in a convenient flask. Nitrogen which has been very carefully saturated with water is led through the solution for 10 min at room temperature by means of a capillary tube.

The saturation of nitrogen with water is attained by bubbling it through two wash bottles, the first containing hot water to ensure saturation.

Methanol is separated from formaldehyde by distillation in the presence of chromotropic acid and is determined as formaldehyde after oxidation[2]. The formaldehyde content in the residue is then established by the method published by Bricker and Vail[3].

No attempt was made to determine how much formaldehyde and methanol could be retained by the water. However, in an experiment in which 120 μg formaldehyde and 450 μg methanol were present, formaldehyde was kept back quantitatively whereas about 3% of the methanol was removed by the stream of nitrogen.

In our specific experiments (to be published elsewhere) it was found necessary to trap the reaction products in a solution of 200 mg of trisodium salt of chromotropic acid instead of in pure water. The reagent acts purely as a buffer for acids present in the mixture which would otherwise cause hydrolysis of the azomethane. The distillation of the methanol is then carried out after acidifying the solution.

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[1] F. C. Whitmore, *Organic Chemistry*, D. van Nostrand Co., New York 1951.
[2] R. N. Boos, *Anal. Chem.*, 20 (1948) 964.
[3] C. E. Bricker and W. A. Vail, *Anal. Chem.*, 22 (1950) 720.

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Plasmocorinth B als Indikator bei komplexometrischen Titrationen

Seitdem die komplexometrische Titration entdeckt wurde[1] bedeutete das Auffinden eines entsprechenden Indikators ein ständiges Problem. Das Murexid entsprach den Erwartungen nicht: die Farbe des Überschlages ist nicht scharf und kann daher mit freiem Auge nicht gut beurteilt werden; deshalb scheint Murexid für einfache Bestimmungen in biologischen Flüssigkeiten nicht geeignet. Neuerdings wurden einige Naphthyl-azo-naphthalin Derivate als Indikatoren bei der Serumkalzium-Bestimmung mit Erfolg verwendet[2-4].

YANAGISAWA[5] und später KINGSLEY UND ROBNETT[6] teilten eine kolorimetrische Bestimmung für Serumkalzium mittels des Farbstoffes Plasmocorinth B (Inabata Industry & Co., Ltd., Osaka, Japan) mit. Dieser Farbstoff ist dem neuerdings beschriebenen Ca-Indikatoren ähnlich mit dem Unterschied, dass dies ein Phenyl-azo-naphthalin Derivat (Plasmocorinth B = Dinatrium Salz der 1-Oxy-4-chlorbenzol-(2-azo-2)-1,8-dioxynaphthalin-3,6-disulfonsäure) ist. Daher wurden Untersuchungen unter der Verwendung dieses Farbstoffes vorgenommen und es konnte festgestellt werden, dass er als Indikator für die komplexometrische Titration von Kalzium und Magnesium sehr gut geeignet ist.

In alkalischem Medium bildet das rote Plasmocorinth B einen farbigen Komplex mit Äthylendiamintetraessigsäure (EDTA); und zwar in der Anwesenheit von Natriumhydroxyd gibt es eine blau-violette, und in derjenigen von Ammoniumhydroxyd, eine

TABELLE I

WIRKUNG VERSCHIEDENER Ca, Mg UND EDTA MENGEN AUF DAS ABSORPTIONSMAXIMUM DES PLASMOCORINTH B

Die Konzentration der verwendeten Ca-, Mg- und EDTA-Lösungen wurde so gewählt, dass gleiche Volumen äquivalente Mengen enthalten sollen.

	10 mg % Plasmocorinth ml	*0.5 N NaOH ml*	*NH_4-puffer* ml*	*0.001 M Ca ml*	*0.001 M Mg ml*	*0.001 M EDTA ml*	*Dest. wasser ml*	*E max. μμ*
1.	1	–	–	–	–	–	11	546
2.	1	1	–	–	–	–	10	554
3.	1	1	–	2	–	–	8	546
4.	1	1	–	2	2	–	6	546
5.	1	1	–	–	–	1	9	572
6.	1	1	–	2	2	1	5	546
7.	1	1	–	2	2	3	3	572
8.	1	1	–	2	2	5	1	572
9.	1	–	1	–	–	–	10	550
10.	1	–	1	–	2	–	8	548
11.	1	–	1	2	2	–	6	548
12.	1	–	1	–	–	1	9	594
13.	1	–	1	2	2	1	5	548
14.	1	–	1	2	2	3	3	548
15.	1	–	1	2	2	5	1	594

* Die Zusammensetzung des HN_4-Puffers ist: 0.83 g NH_4Cl + 12 ml conc. NH_4OH + dest. Wasser ad 100 ml.

intensiv blaue Farbe. Wenn eine Ca und Mg enthaltende Lösung in der Anwesenheit von NaOH mit EDTA titriert wird, so reagiert das EDTA nach Bindung der äquivalenten Menge des Kalziums mit Plasmocorinth B; diese Reaktion wird durch die Anwesenheit von Mg nicht gestört. In der Anwesenheit von NH_4OH dagegen, bildet das Plasmocorinth B mit dem EDTA erst nach der gemeinsamen Bindung der äquivalenten Menge von Ca *und* Mg (Tabelle I). In erstem Falle kann durch die Zugabe von überschüssigem Ca, und in dem zweiten, durch diejenige von überschüssigem Ca *oder* Mg die ursprüngliche Farbe des Indikators zurückgewonnen werden. (Ähnlicherweise kann der labile Indikator–EDTA Komplex gespalten werden wenn das pH des Mediums herabgesetzt wird). In beiden Fällen ist die Farbe des Überschlages scharf; zwischen der eigenen Farbe des Indikators und derjenige des Plasmocorinth B–EDTA Komplexes besteht ein leicht beurteilbarer Unterschied (Fig. 1 und 2).

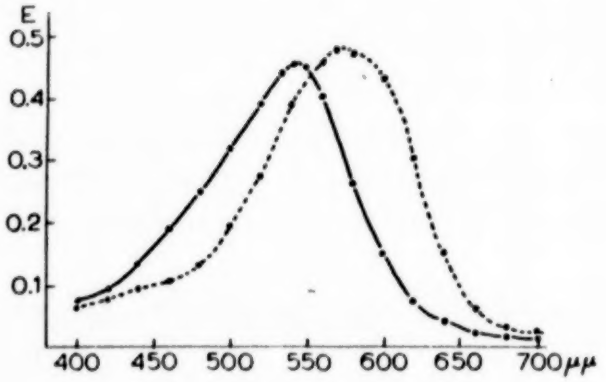

Fig. 1. Die Absorptionskurve des Plasmocorinth B und des Plasmocorinth B-EDTA Komplexes in NaOH-Medium. (—.—.—. = Plasmocorinth B + NaOH + Ca + Mg, ... = Plasmocorinth B + NaOH + Ca + Mg + überschüssiges EDTA).

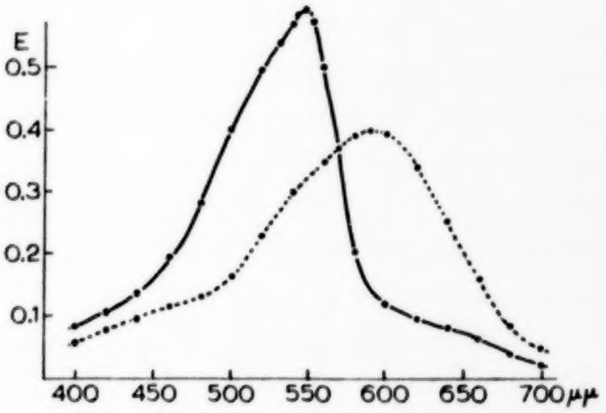

Fig. 2. Die Absorptionskurve des Plasmocorinth B und des Plasmocorinth B-EDTA Komplexes in NH_4OH-Medium. (—.—.—. = Plasmocorinth B + NH_4OH + Ca + Mg, ... = Plasmocorinth B + NH_4OH + Ca + Mg + überschüssiges EDTA).

Mit der Verwendung dieses Prinzips gelang es uns eine einfache Methode auszuarbeiten, mit welcher der Ca- und Mg-Gehalt des Serums, des Liquors und des Harns in kurzer Zeit genau bestimmt werden kann.

Verfasser sprechen der Firma Inabata Industry & Co., Ltd., ihren aufrichtigen Dank für die Überlassung des benötigten Plasmocorinth B aus.

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[1] G. Schwarzenbach, W. Biedermann und F. Bangerter, *Helv. Chim. Acta*, 29 (1946) 811.
[2] H. Diehl und J. L. Ellingboe; *Anal. Chem.*, 28 (1956) 882.
[3] J. Patton und W. Reeder; *Anal. Chem.*, 28 (1956) 1026.
[4] G. P. Hildebrand und C. N. Reilley; *Anal. Chem.*, 29 (1957) 258.
[5] F. Yanagisawa, *J. Biochem.*, 42 (1955) 3.
[6] G. R. Kingsley und O. Robnett; *Am. J. Clin. Pathol.*, 27 (1957) 223.

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REVUES DE LIVRE

Handbuch der Papierchromatographie. 2 Bände. Herausgegeben von DR. IVO M. HAIS und DR. KAREL MACEK, beide Forschungsinstitut für Pharmazie und Biochemie Prag. Uebersetzung nach der zweiten, überarbeiteten und erweiterten tschechischen Auflage von J. LIEBSTER, Prag.

Band I: Grundlagen und Technik. Unter Mitarbeit von 20 Fachwissenschaftlern. VEB Gustav Fischer Verlag, Jena 1958, mit 242 zum Teil farb. Abb. im Text. XXIV + 860 S. gr. 8°. Ganzleinen DM 58,40.

La chromatographie sur papier a déjà fait l'objet d'assez nombreux traités, écrits par d'éminents spécialistes. Aussi, la publication d'un livre nouveau dans ce domaine demande-t-elle bien de qualités à son auteur, si ce dernier désire obtenir quelque succès auprès du public.

Or, voici qu'un comité de vingt-deux savants tchécoslovaques a entrepris la préparation d'un traité de chromatographie sur papier, dans l'ambition que leur oeuvre, dépassant les limites d'un simple exposé théorique et pratique du sujet, puisse permettre aux chimistes non initiés de se familiariser avec les différentes techniques actuelles et leur offrir la possibilitè de les appliquer sans trop de difficultés.

Ce but fort louable par ailleurs est-il atteint? Nous croyons pouvoir répondre oui. En effet, cet excellent ouvrage contient un choix très judicieux des méthodes les plus importantes au point de vue théorique et pratique. La bibliographie a été consultée jusqu'à la fin de 1955, mais les principales publications parues en 1956 y figurent également. De toute manière, un répertoire bibliographique complet fera l'objet d'un second volume annoncé pour le début 1960.

Après une brève introduction historique, un exposé, clair, sur la théorie de la méthode permet d'aborder les principes fondamentaux avec un minimum de formules mathématiques et d'une manière absolument satisfaisante. Vient ensuite le chapitre concernant la technique générale; les opérations sont décrites successivement dans le même ordre que lors de la préparation d'un chromatogramme. A la fin de la partie générale, l'on trouve encore deux petits chapitres consacrés à la chromatographie des produits radioactifs et à la chromatographie préparative sur papier et sur colonne de cellulose.

Suit la partie spéciale, traitant de très nombreuses classes de corps organiques et donnant la préférence aux dérivés d'importance biologique ou pharmaceutique. A la fin, un petit chapitre s'occupe des colorants et 90 pages seulement sont consacrées à l'analyse minérale. C'est peut-être l'unique point faible du livre.

L'exposé pratique est encore suivi de deux listes: la première contient les réactifs servant à identifier les ,,spots''; la seconde ,un recueil de méthodes concernant les traitements divers du papier, un choix de solvants et plusieurs exemples d'analyse quantitative.

Ajoutons encore deux mots sur la présentation parfaite de l'ouvrage et félicitons le traducteur qui le rend ainsi accessible à un public beaucoup plus large. Persuadés de sa valeur, nous recommandons ce livre à tous ceux qui travaillent en chimie organique croyant qu'il constituera une aide précieuse pour leurs recherches.

I. KAPÉTANIDIS (Genève)

Besser spat als nie, par CLÉMENT DUVAL, cours d'allemand scientifique pour les débutants. 6° Éd. – Edition CNRS, Paris 1958, 103 pages, Fr. 500.—.

Ce cours d'allemand scientifique, conçu en 1945–'46 pour l'instruction des chercheurs et aides techniques, et qui est devenu depuis cette époque un cours régulier comprenant 25 leçons en est aujourd'hui à sa sixième édition, complètement remanié. Ceci prouve d'une part qu'il répond à un besoin réel, et d'autre part, que par suite de l'élargissement considérable du vocabulaire le livre est d'une utilité incontestable aussi bien pour les chimistes, que pour les physiciens, les botanistes, les pharmaciens, etc.

Chacune des 25 leçons ne demande, au dire de l'auteur, que 3 heures d'étude. Ceci permet de s'approprier en peu de temps les bases essentielles de la grammaire, de la syntaxe et un vocabulaire technique suffisant pour la lecture des périodiques allemands et pour la traduction de textes techniques, comme celui de la page 100 qui forme l'examen de fin de cours.

Ce livre peut être recommandé vivement à tous ceux, qui par leurs travaux de recherches éprouvent le besoin d'améliorer leurs connaissances de la langue allemande.

G. VAN DER KELEN (Gand)

REVUE DE LIVRE

Electroanalytical Chemistry, par **James J. Lingane**. 2nd Ed., revised and enlarged. Interscience Publishers Inc., New York 1958, 669 pp., $ 14.50.

Le Prof. Lingane vient de faire paraître la seconde édition de son livre ,,*Electroanalytical Chemistry*''. Considérablement augmenté, 669 pp. au lieu de 448, il renferme plusieurs chapitres nouveaux.

Citons l'analyse polarographique avec comme paragraphes: Appareillage et technique, caractérisation du courant limite avec l'électrode à goutte, calibrage de l'électrode à goutte en polarographie, équations des ondes polarographiques et potentiel de demi-onde. L'ampérométrie et les titrations ampérométriques font aussi l'objet d'un nouveau chapitre dans lequel l'auteur traite de l'ampérométrie avec une ou deux électrodes polarisables. Signalons encore le chapitre ayant pour objet la titration coulométrique à courant constant et la chronopotentiométrie, théorie, méthodologie, appareillage et applications analytiques. La plupart des anciens chapitres ont été complétés. L'auteur ne donne pas une bibliographie complète, il a choisi parmi les très nombreuses publications de ces dernières années (jusqu'en 1958) celles qui sont susceptibles d'illustrer son exposé. Celui-ci est présenté de façon claire, avec un souci constant de simplification. Il est accompagné de nombreuses applications décrites avec le plus grand soin. La partie théorique est traitée de façon originale et suggestive et ne fait appel qu'à des considérations physico-chimiques élémentaires. On pourrait reprocher à l'auteur d'avoir surchargé son ouvrage d'une série de schémas qui présentent peu d'intérêt pour la plupart des chimistes analystes, mais ceci n'enlève rien à la valeur de ce livre de choix qui est fort bien présenté et illustré de nombreuses figures.

D. **Monnier** (Genève)

BUCHBESPRECHUNG

Handbuch der Analytischen Chemie, herausgegeben von W. **Fresenius und** J. **Jander**, Springer Verlag, Berlin 1958, Dritter Teil: Quantitative Bestimmungs- und Trennungsmethoden, Band VI b*α*, Elemente der sechsten Nebengruppe (Chrom), LV, 411 S., DM 104.—, Ganzleinen DM 108.—.

Die Verfasser behandeln zuerst die Bestimmungsmöglichkeiten des Chroms und orientieren über deren Eignung. Besondere Berücksichtigung erhalten einzelne theoretische Betrachtungen z.B. die der modernen Oxydationsmethoden durch Überchlorsäure.

Das Buch fährt fort mit den Kapiteln der gravimetrischen Bestimmungsmethoden des 3- und 6-wertigen Chroms. Die genauen Arbeitsvorschriften machen das Buch für den Praktiker und für den Theoretiker interessant.

Auf den gleichen Principien sind auch die Kapitel der titrimetrischen Chrombestimmung aufgebaut. Speziell sorgfältig werden dabei die direkten und indirekten iodometrischen und ferrometrischen Titrationen behandelt. Der Benützer des Buches wird dabei auch auf die, in dem Falle des Chroms, so wichtige Frage der Endpunktbestimmung durch Redoxindikatoren und elektrometrische Methoden aufmerksam gemacht. Die Bemerkungen bezüglich der Genauigkeit der Methoden, der eventuellen Indikatorenkorrekturen und der störenden Stoffe sind nach unserem Dafürhalten besonders wertvoll.

Sehr modern sind auch die folgenden Kapitel der physikalisch-chemischen Methoden; der Kolorimetrie, Photometrie, Polarographie und der spektral-analytischen Analyse. Auch hier begrüssen wir ganz besonders die genauen detaillierten und sehr vollständigen Angaben.

Der letzte Teil des Buches behandelt die Trennungen des Chroms (Eisen, Aluminium, Nickel, Titan, usw.) und die speziellen Methoden der Chrombestimmung in Stahl, den verschiedensten Legierungen, den Erzen, im Abwasser, in organischen Verbindungen in Gasen und Stauben usw.

Abschliessend können wir sagen, dass das Buch ein modernes und wohl vollständigste Werk der Chromanalyse darstellt. Wir können es wegen seinem klaren Aufbau und Vollständigkeit allen analytisch Interessierten bestens empfehlen.

H. **Keller** (Genf)

SOME QUANTITATIVE REMARKS ON EXTRACTION EQUILIBRIA. I

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INTRODUCTION

Solvent extraction has been used for a long time but originally seemed to be of interest to organic chemists only; the quantitative treatment of the relatively simple equilibria involved in organic work is well-known and does not cause any difficulties. Although solvent extraction in inorganic chemistry has also been known for a long time, it did not become commonly used until about 1940.

The general application of solvent extraction in inorganic analysis is hindered because the complicated equilibria make quantitative treatment either too simplified or too intricate for practical use. It is our opinion that more extensive use would be made of this attractive technique if the fundamental principles could be expressed in a quantitative form which would not present undue mathematical difficulties, but which would not be so simplified that only worthless results could be obtained. We therefore developed expressions which we believe avoid both drawbacks.

Among the attractive aspects of solvent extraction in inorganic analysis are:

a) the completeness of the separations obtained,

b) the selectivity of the separations, which can often be influenced in various ways (pH, complexing agents), and

c) the fact that the residual aqueous solution can easily be used for the determination of other ions, with or without using solvent extraction.

It should be stressed that extraction is primarily a method of separation. If the extracted component is intensely coloured, a quantitative determination can be done but this should not be the criterion of the usefulness of an extraction. However, among the increasing number of articles on solvent extraction, relatively few deal with the extraction of colourless compounds as a separation prior to some appropriate method of determination.

As a rule, the description of extraction phenomena is only incidental and far from complete. Often the essential data are missing, such as the reagent concentration, the volumes of the aqueous and solvent phases, and the number of successive extractions. In this respect, many of the published data appear to be conflicting. Table I which shows some data collected from papers dealing with extraction with oxine and chloroform may serve as an example.

Some quantitative considerations on extraction equilibria have already been published, but these have not yet led to a satisfactory understanding of the functions of all the important factors.

TABLE I

Element	*Complete extraction*	*pH at which incomplete extraction is said to take place*	*No extraction*	*References*
Al	6.6 ± 0.2		2.8	1
	8.9			2
	4.3 – 4.6	2.5 – 4.3; 4.6 – 6		3
	5			4
Bi	8.9			2
	4 – 5.3	2 – 4; > 5.3		3
Cu	2.8			1
	8.9			2
	> 2.5	1.6 – 2.5		3
	2.5			5
Ni	2.8			1
	8.9			2
	> 6.8	2.6 – 6.8		3
UO_2	8.9			2
	3			6
Fe	2.8			1
	8.9			2
	2 – 3	1.5 – 2; > 3.5		3
	5			4
	4.5			7

In some cases a careless use of the expressions might lead to wrong conclusions. In FLAGG[8] is given the expression:

$$\frac{\mathrm{MDz_2}(o)}{\mathrm{M^{+2}}(w)} = K\frac{\mathrm{HDz^2}(o)}{(\mathrm{H^+})^2(w)},$$

originally published by KOLTHOFF AND SANDELL[9], in which $\mathrm{MDz_2}(o)$ represents the concentration of a metaldithizonate and $\mathrm{HDz}(o)$ the concentration of dithizone (both in the organic phase), $\mathrm{M^{+2}}(w)$ the concentration of metal ions and $\mathrm{H^+}(w)$ the concentration of hydrogen ions (both in the aqueous phase); K is a constant.

The objections to this expression are:

1. The quotient

$$\frac{\mathrm{MDz_2}(o)}{\mathrm{M^{+2}}(w)}$$

does not show clearly the degree of separation obtained because the volumes of both phases must be known for this purpose. It is more correct to use the ratio of both quantities, expressed in mg moles and mg ion, rather than concentrations.

2. The term $\mathrm{HDz}(o)$ depends on the total amount of dithizone, the pH, the volumes of both phases and the organic solvent chosen.
3. The expression might lead to the wrong conclusion, *i.e.* that an extraction would be promoted by increasing $\mathrm{HDz}(o)$. This is only true, however, if $\mathrm{HDz}(w)$ and $\mathrm{Dz^-}(w)$ are also increased, which means a higher total reagent concentration. With a given amount of reagent, however, it is of advantage to decrease $\mathrm{HDz}(o)$, which can be effected by increasing the pH.

Analogous expressions have been published by FURMAN, MASON AND PECOLA[10], by SANDELL AND CUMMINGS[11] and by MORRISON AND FREISER[12].

A different expression is given by IRVING AND WILLIAMS[13], who derive the apparently simple expression:

$$x = 50(1 - \tanh 1.1513\, n\, \Delta\, \mathrm{pH}),$$

where x represents the percentage of metal ion extracted and n the valency of the metal ion considered.

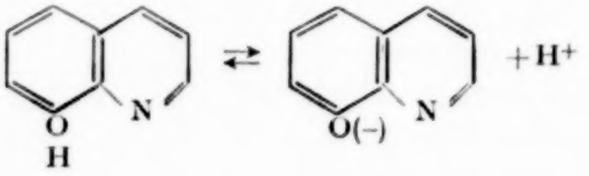
Δ pH represents pH − pH$_{\frac{1}{2}}$, in which pH is the actual pH considered and pH$_{\frac{1}{2}}$ is the pH value at which 50% of the metal ion is extracted. This pH$_{\frac{1}{2}}$ is only constant as long as the concentration of the reagent and the volumes of both phases are kept constant.

In this paper, we shall describe the qualitative pattern of the reactions involved in solvent extraction, and elaborate that pattern quantitatively after making some restrictions as to the universal validity of the resulting expressions.

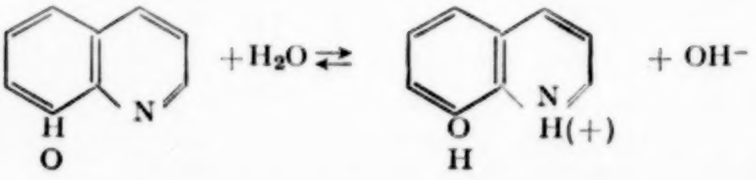
During the extraction of a metal ion M^+ with an organic reagent HR and a non-miscible solvent, the following reactions have to be considered. (For the sake of simplicity the metal ion is first taken as monovalent.)

1. The reagent dissociates: $HR \rightleftarrows H^+ + R^-$, as determined by a dissociation constant K^a_{HR}.
2. The metal ion reacts with the reagent anion: $M^+ + R^- \rightleftarrows MR$, in an amount determined by the solubility product L_{MR}.
3. The "chelate" is extracted by the immiscible solvent, $MR_w \rightleftarrows MR_o$, in an amount determined by a distribution coefficient E_{MR}.

   The following reactions work against extraction:
4. The undissociated reagent is extracted by the solvent $HR_w \rightleftarrows HR_o$, in an amount determined by a distribution coefficient E_{HR}.
5. The reagent can also react otherwise than in reaction 1, *e.g.* $HR + H_2O \rightleftarrows H_2R^+ + OH^-$, which is determined by a dissociation constant K^b_{HR}. This applies, for example, to oxine, where the dissociation



occurs as well as the reaction



which becomes more important in acid solutions.

6. The metal ion can be fixed by other ions besides R^-, (*e.g.* by hydroxyl, fluoride, or tartrate ions etc.), in amounts determined by the complex constants. This

is the most important reaction when dealing with diethyldithiocarbamate (pH always above 5, often in the presence of tartrate, cyanide, EDTA).
Schematically:

$$\begin{tikzcd}
MX \arrow[r, shift left, "K_c"] \arrow[r, shift right, leftarrow] & X^- + M^+ + & R^- \arrow[r, shift left, "L_{MR}"] \arrow[r, shift right, leftarrow] & MR_w \arrow[r, shift left, "E_{MR}"] \arrow[r, shift right, leftarrow] & MR_o \\
 & & + & & \\
 & & H^+ \arrow[d, shift right, "K^{a}_{HR}"'] \arrow[d, shift left, leftarrow] & & \\
OH^- + H_2R^+ \arrow[rr, shift left, "K^{b}_{HR}"] \arrow[rr, shift right, leftarrow] & & HR_w + H_2O \arrow[d, shift right, "E_{HR}"'] \arrow[d, shift left, leftarrow] & & \\
 & & HR_o & &
\end{tikzcd}$$

The problem can be split into two parts:

1. Under definite conditions what is the concentration of R^- in the aqueous phase?
2. How much of the metal ion M^+ remains in the aqueous phase when it contains the amount of R^- found under 1?

The following restrictions and assumptions will be made:

1. No complexes are formed (the reaction $M^+ + X^- \rightleftarrows MX$ does not take place).
2. A large excess of reagent is used.
3. Only those systems where the compound MR is soluble in the solvent used but almost insoluble in water will be considered.

It is well-known that free ions are not extracted to a measurable extent.

THE CALCULATION OF R^-

The problem

An aqueous solution of volume V_w contains a mg ion of a metal ion. Its concentration a/V_w is written as A.

An organic reagent HR (b mg moles) is added, the concentration of which, b/V_w is written as B. It is assumed that $B \gg A$. The reagent is amphoteric, and the dissociation constants are K^{a}_{HR} (dissociation as an acid) and K^{b}_{HR} (dissociation as a base). It is considered as a monovalent acid or base.

V_o ml of immiscible solvent, in which MR and possibly undissociated HR are soluble, is used for extraction. The quotient V_w/V_o is represented by f. The distribution coefficient E_{HR} is defined as

$$E_{HR} = \frac{HR_o}{HR_w} = \frac{\text{concn. undiss. HR org. phase}}{\text{concn. undiss. HR aq. phase}}.$$

Resolution

An excess of reagent $= b$ mg moles is present in 4 forms:

1. HR_w, the undissociated reagent in the aqueous phase,
2. HR_o, the undissociated reagent in the organic phase,
3. H_2R^+, reagent dissociated as a base (in the aqueous phase),
4. R^-, reagent, dissociated as an acid (in the aqueous phase).

The equations are:

$$K^{a}_{\mathrm{HR}} = \frac{\mathrm{H}^{+} \cdot \mathrm{R}^{-}}{\mathrm{HR}_{w}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$\mathrm{K}^{b}_{\mathrm{HR}} = \frac{\mathrm{OH}^{-} \cdot \mathrm{H_2R}^{+}}{\mathrm{HR}_{w}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$E_{\mathrm{HR}} = \frac{\mathrm{HR}_{o}}{\mathrm{HR}_{w}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Now of course:

$$b = [\mathrm{HR}_{w}] + [\mathrm{HR}_{o}] + [\mathrm{H_2R}^{+}] + [\mathrm{R}^{-}] \quad \ldots\ldots\ldots \quad (4)^{*}$$

and, as $B = b/V_{w}$:

$$B = \mathrm{HR}_{w} + \frac{E_{\mathrm{HR}}}{f} \cdot \mathrm{HR}_{w} + \mathrm{H_2R}^{+} + \mathrm{R}^{-} \quad \ldots\ldots\ldots \quad (4a)$$

Using equations (1) to (3), all terms can be expressed as a function of R^{-}.

$$B = \frac{\mathrm{H}^{+}}{K^{a}_{\mathrm{HR}}} \cdot \mathrm{R}^{-} + \frac{E_{\mathrm{HR}}}{f} \cdot \frac{\mathrm{H}^{+}}{K^{a}_{\mathrm{HR}}} \cdot \mathrm{R}^{-} + \frac{K^{b}_{\mathrm{HR}}}{\mathrm{OH}^{-}} \cdot \frac{\mathrm{H}^{+}}{K^{a}_{\mathrm{HR}}} \cdot \mathrm{R}^{-} + \mathrm{R}^{-}$$

$$\text{or } B = \mathrm{R}^{-} \left\{ \frac{\mathrm{H}^{+} \cdot f \cdot \mathrm{OH}^{-} + E_{\mathrm{HR}} \cdot \mathrm{H}^{+} \cdot \mathrm{OH}^{-} + fK^{b}_{\mathrm{HR}} \cdot \mathrm{H}^{+} + K^{a}_{\mathrm{HR}} \cdot f \cdot \mathrm{OH}^{-}}{K^{a}_{\mathrm{HR}} \cdot f \cdot \mathrm{OH}^{-}} \right\} \quad \ldots\ldots \quad (5)$$

or, multiplying the numerator and denominator by H^{+} and resolving R^{-}, since $\mathrm{H}^{+} . \mathrm{OH}^{-} = K_{w}$

$$\mathrm{R}^{-} = \frac{K^{a}_{\mathrm{HR}} \cdot f \cdot K_{w} \cdot B}{\mathrm{H}^{+} K_{w} (f + E_{\mathrm{HR}}) + f\left\{K^{b}_{\mathrm{HR}} (\mathrm{H}^{+})^{2} + K^{a}_{\mathrm{HR}} \cdot K_{w}\right\}} \quad \ldots\ldots\ldots\ldots \quad (6)$$

This is the most general expression for R^{-}. Sometimes, this expression can be simplified. For example, if the reagent is not amphoteric, $K^{b}_{\mathrm{HR}} = 0$, and accordingly:

$$\mathrm{R}^{-} = \frac{K^{a}_{\mathrm{HR}} \cdot f \cdot B}{\mathrm{H}^{+}(f + E_{\mathrm{HR}}) + fK^{a}_{\mathrm{HR}}}.$$

If the reagent is also a very weak acid, or if we consider strongly acid solutions ($K^{a}_{\mathrm{HR}} \ll \mathrm{H}^{+}$), then, because $(f + E_{\mathrm{HR}}) \leqslant f$,

$$\mathrm{R}^{-} = \frac{K^{a}_{\mathrm{HR}} \cdot f \cdot B}{\mathrm{H}^{+}(f + E_{\mathrm{HR}})}.$$

THE CALCULATION OF THE EXTRACTION ERROR

It is assumed that extraction of a metal chelate can only take place if a certain amount of undissociated metal chelate is formed in the aqueous phase. The compound MR should be dissociated incompletely and accordingly there is a dissociation constant:

$$K_{\mathrm{MR}} = \frac{\mathrm{M}^{+} \cdot \mathrm{R}^{-}}{\mathrm{MR}_{w}}.$$

---

* Square brackets refer to quantities (in mg moles or mg ion), the other symbols to concentrations.

In the presence of solid MR, the aqueous and the organic phase are both saturated, hence for the partition coefficient:

$$E_{\mathrm{MR}} = \frac{\mathrm{MR}_o \text{ sat.}}{\mathrm{MR}_w \text{ sat.}}. \text{ But as } E_{\mathrm{MR}} = \frac{\mathrm{MR}_o \text{ unsat.}}{\mathrm{MR}_w \text{ unsat.}},$$

it follows that

$$\frac{\mathrm{MR}_o \text{ sat.}}{\mathrm{MR}_w \text{ sat.}} = \frac{\mathrm{MR}_o \text{ unsat.}}{\mathrm{MR}_w \text{ unsat.}} \quad \text{(7)*}$$

Consider the extraction of a metal ion M^+ in the presence of a definite amount of R^-. In an aqueous solution saturated with regard to MR:

$$K_{\mathrm{MR}} = \frac{M^+ \cdot R^-}{\mathrm{MR}_w \text{ sat.}} \text{ and } M^+ \cdot R^- = L_{\mathrm{MR}}.$$

K_{MR} is readily seen to be $K_{\mathrm{MR}} = L_{\mathrm{MR}}/\mathrm{MR}_w$ sat.

Now, in most extractions the aqueous phase is unsaturated with regard to MR, hence in the aqueous phase:

$$K_{\mathrm{MR}} = \frac{M^+ \cdot R^-}{\mathrm{MR}_w \text{ unsat.}},$$

$$\text{or } M^+ \cdot R^- = K_{\mathrm{MR}} \cdot \mathrm{MR}_w \text{ unsat.} = L_{\mathrm{MR}} \cdot \frac{\mathrm{MR}_w \text{ unsat.}}{\mathrm{MR}_w \text{ sat.}}$$

or substituting (7):

$$M^+ \cdot R^- = L_{\mathrm{MR}} \cdot \frac{\mathrm{MR}_o \text{ unsat.}}{\mathrm{MR}_o \text{ sat.}}$$

$$\text{or } M^+ = \frac{1}{R^-} \cdot L_{\mathrm{MR}} \frac{\mathrm{MR}_o \text{ unsat.}}{\mathrm{MR}_o \text{ sat.}} \quad (8)$$

In precipitation reactions $M^+ \cdot R^- = L_{\mathrm{MR}}$ and thus:

$$M^+ = \frac{1}{R^-} \cdot L_{\mathrm{MR}} \quad (9)$$

From equations (8) and (9), it can be seen that an ion is more completely removed from a solution by extraction than by precipitation because

$$\frac{\mathrm{MR}_o \text{ unsat.}}{\mathrm{MR}_o \text{ sat.}} < 1.$$

Strictly speaking, the amount of metal ion which is not removed by precipitation is:

$$M^+ + \mathrm{MR}_w \text{ sat.} = \frac{1}{R^-} \cdot L_{\mathrm{MR}} + \mathrm{MR}_w \text{ sat.}$$

The amount of ion which is not removed by extraction is $M^+ + \mathrm{MR}_w$ unsat., and this can be written as:

$$\frac{1}{R^-} \cdot L_{\mathrm{MR}} \cdot \frac{\mathrm{MR}_o \text{ unsat.}}{\mathrm{MR}_o \text{ sat.}} + \mathrm{MR}_w \text{ sat.} \frac{\mathrm{MR}_o \text{ unsat.}}{\mathrm{MR}_o \text{ sat.}} \text{ or}$$

$$\left\{ \frac{1}{R^-} \cdot L_{\mathrm{MR}} + \mathrm{MR}_w \text{ sat.} \right\} \frac{\mathrm{MR}_o \text{ unsat.}}{\mathrm{MR}_o \text{ sat.}}.$$

---

* As a rule MR_o sat. is not large. For oxinates in chloroform we found values of 10^{-3} – 10^{-2}, so we may regard the saturated solutions as dilute ones to which the corresponding laws apply unrestrictedly.

Thus the conclusion concerning more complete removal by extraction still applies. In the following part it is assumed that MR_w is always negligible compared to M^+. KOLTHOFF AND SANDELL[9] also use this supposition. IRVING AND WILLIAMS[13] object to it, but use a neglection which on further consideration turns out to be based on the same supposition. The good agreement found by IRVING AND WILLIAMS between the calculated and the experimentally found extractions proves the validity of this neglection at least for the systems investigated.

The concentration of the unextracted metal ion M^+ was found to be

$$M^+ = \frac{L_{MR} \cdot MR_o \text{ unsat.}}{R^- \cdot MR_o \text{ sat.}} \quad \ldots\ldots\ldots\ldots \quad (8)$$

If the term m^+ res. (idual) is introduced for the number of mg ions of metal that are not extracted, then $m^+ \text{ res.} = V_w M^+$.

$$m^+ \text{ res.} = \frac{V_w \cdot L_{MR} \cdot MR_o \text{ unsat.}}{R^- \cdot MR_o \text{ sat.}} \quad \ldots\ldots\ldots\ldots \quad (10)$$

$$\text{Now } MR_o \text{ unsat.} = \frac{a - m^+ \text{ res.}}{V_o} \quad \ldots\ldots\ldots\ldots \quad (11)$$

and substituting (11) in (10):

$$m^+ \text{ res.} = \frac{V_w \cdot L_{MR}\,(a - m^+ \text{ res.})}{V_o R^- \cdot MR_o \text{ sat.}} = \frac{fL_{MR} \cdot a}{R^- \cdot MR_o \text{ sat.}} - \frac{fL_{MR} \cdot m^+ \text{ res.}}{R^- \cdot MR_o \text{ sat.}}$$

$$\text{or } m^+ \text{ res.} \left\{ 1 + \frac{fL_{MR}}{R^- \cdot MR_o \text{ sat.}} \right\} = \frac{f \cdot a \cdot L_{MR}}{R^- \cdot MR_o \text{ sat.}}$$

Hence, for the unextracted fraction of the metal ion or "extraction error":

$$\frac{m^+ \text{ res.}}{a} = \frac{fL_{MR}}{R^- \cdot MR_o \text{ sat.} + fL_{MR}} \quad \ldots\ldots\ldots\ldots \quad (12)$$

This equation, together with (6) completely describes the extraction equilibria. Substitution of R^- from eq. (6) in (12) leads to a very complicated form. It will be shown in a later paper that this substitution is not necessary. For n-valent metal-ions, we can derive in exactly the same way:

$$\frac{m^{+n} \text{ res.}}{a} = \frac{fL_{MR_n}}{(R^-)^n \cdot MR_{no} \text{ sat.} + fL_{MR_n}} \quad \ldots\ldots\ldots \quad (12a)$$

SUMMARY

Two equations are derived, showing the quantitative relationship between the course of a solvent extraction and the factors involved. These equations only contain independent variables.

RÉSUMÉ

Par deux équations dérivées, l'auteur donne une interprétation quantitative d'une extraction par solvant, en fonction des différents facteurs qui peuvent intervenir.

ZUSAMMENFASSUNG

Es wird gezeigt, dass der Einfluss bestimmter Faktoren auf den quantitativen Verlauf einer Extraktion mit Lösungsmitteln durch zwei Gleichungen ausgedrückt werden kann.

REFERENCES

[1] O. A. Kenyon and H. A. Bewick, *Anal. Chem.*, 24 (1952) 1826.
[2] L. Silvermann, L. Moudy and D. W. Hawley, *Anal. Chem.*, 25 (1953) 1369.
[3] Th. Moeller, *Ind. Eng. Chem., Anal. Ed.*, 15 (1943) 346.
[4] H. J. Cluley, *Analyst*, 79 (1954) 567.
[5] F. A. Pohl and H. Demmel, *Anal. Chim. Acta*, 10 (1954) 554.
[6] B. Hök, *Svensk Kem. Tidskr.*, 65 (1953) 106.
[7] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, 8 (1936) 336.
[8] J. Flagg, *Organic Reagents*, Interscience Publishers, Inc., New York 1948.
[9] I. M. Kolthoff and E. B. Sandell, *J. Am. Chem. Soc.*, 63 (1941) 1906.
[10] N. H. Furman, W. B. Mason and J. S. Pecola, *AnalChem.* ,21 (1949) 1325.
[11] E. B. Sandell and Ph. H. Cummings, *Anal. Chem.*, 21 (1949) 1356.
[12] G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*, John Wiley & Sons Inc., New York 1957.
[13] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, (1949) 1841.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM USING 4-METHYL-1,2-CYCLOHEXANEDIONEDIOXIME*

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INTRODUCTION

Many reagents have been proposed for the spectrophotometric determination of palladium. The reducing properties of mercury(I) chloride have been used to determine submicrogram quantities of palladium by observing the color and opaqueness of the palladium metal deposited on the mercury(I) chloride[1,2]. Palladium has also been determined by estimating its catalytic effect on the reduction of nickel(II) by sodium hypophosphite[3]. Hydrobromic acid[4], iodide[5-8], tin(II) chloride[9], and thiocyanate[10,11] have also been suggested as colorimetric reagents.

Some of the organic reagents which have been reported for the determination of palladium are: 4-nitrosoresorcinol[12], *p*-dimethylaminobenzylidenerhodanine[13,14], compounds containing the *p*-nitrosoamino groups[15-17], 2-mercapto-4,5-dimethylthiazol[18], 1-nitroso-2-naphthol[19], 2-nitroso-1-naphthol[20], rubeanic acid[21], ethylenediaminetetraacetic acid (EDTA)[22], thiourea[23], and substituted acetylenes[24]. Various oximes have also been reported for the colorimetric determination of palladium[25-27].

Many of the reagents mentioned above do not possess all the desired properties of an ideal colorimetric reagent[28]. Sogani and Bhattacharyya[29] have proposed 3-hydroxy-1-*p*-sulfonatophenyl-3-phenyltriazine as a colorimetric reagent for palladium, and they report it to be better and more ideal than any of the reagents mentioned previously in the literature. Recently Majumdar and Chakrabartty suggested 2,5-dimercapto-1,3,4-thiodiazole (Bismuthiol I)[30] and 5-mercapto-3-phenyl-2-thio-1,3,4-thiodiazolone-2 (Bismuthiol II)[31] as new reagents for the determination.

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KODAMA[32] used *o*-nitrosoresorcinol monomethyl ether as a colorimetric reagent for palladium and rhodium. Palladium is heated with perchloric or sulfuric acid until fumes are evolved. The solution is transferred to a separatory funnel and extracted with chloroform. The absorbance of the chloroform phase is measured at 420 mμ.

A procedure employing nickel or potassium dialkyl- and diaryldithiophosphates for the determination of palladium was published by BUSEV AND IVANIUTIN[33]. The complex formed is insoluble in strong acids such as hydrochloric or sulfuric, but can be extracted with chloroform or carbon tetrachloride. The maximum absorption of the complex in carbon tetrachloride is at 295 mμ and is used for spectrophotometric determinations in the range of 0.014–0.090 mg Pd/25 ml; however, the absorbance of more concentrated solutions (0.16–1.1 mg Pd/25 ml) is measured spectrophotometrically at 340 mμ.

Although the reactions of palladium with *vic*-dioximes have been known for a long time, very few colorimetric methods have been published employing them. Those dioximes which have been used are methylglyoxime[25,26,34], dimethylglyoxime[35], and α-furildioxime[36].

4-Methyl-1,2-cyclohexanedionedioxime (4-methylnioxime) can be easily prepared[37] and has been reported to be an excellent gravimetric reagent for palladium[38]. The purpose of this study was to determine the merits of this compound as a colorimetric reagent.

APPARATUS AND REAGENTS

Absorbance measurements were made with a Beckman Model DU spectrophotometer using 1-cm silica cells. A Cary Model 12 recording spectrophotometer was used to scan the spectra of the complexes and reagents. A Beckman Model G pH meter was used for pH studies. The volumetric glassware employed was Kimble Normax and Pyrex class "A". 4-Methyl-1,2-cyclohexanedionedioxime: this compound was prepared in this laboratory[37] and a saturated aqueous solution was used. Standard palladium solution: a solution was prepared by dissolving 0.8236 g of reagent-grade palladium chloride in hydrochloric acid and diluting to 2 l. This solution was standardized gravimetrically using 1,2-cyclohexanedionedioxime according to the procedure of VOTER, BANKS, AND DIEHL[39]. The concentration of palladium was found to be $2.11 \cdot 10^{-3}$ moles/l.

Buffer solution: a hydrochloric acid–potassium chloride buffer solution was prepared by mixing 5.30 ml of 0.2 *N* HCl and 25 ml of 0.2 *N* KCl solutions and diluting to 100 ml.

Other chemicals used were reagent-grade quality.

EXPERIMENTAL WORK

HOOKER[40] found that palladium could be determined by the suspension–spectrophotometric method proposed by FERGUSON AND BANKS[41] for the determination of nickel. Gum arabic is added to the solution to stabilize the suspension of the precipitate. Highly colored ions seriously interfere in this method. However, if gum arabic is omitted and the precipitate allowed to form and then extracted, a very sensitive method results.

The precipitate of bis (4-methylnioximato-*N*,*N'*) palladium(II) was found to be soluble in chloroform and to have an absorption band at 280 mμ. Neither 4-methylnioxime nor chloroform shows appreciable absorption at this wavelength.

For optimum extraction the pH of the aqueous phase should be between 0.7 and 5.0. The solution should be prepared 60 min prior to extraction.

It was observed that the chloroform phase was stable for only 3 h after being equilibrated with an aqueous phase which was adjusted to pH 2 with hydrochloric acid. However, if the aqueous phase is adjusted to pH 2 with a hydrochloric acid–potassium chloride buffer, the chloroform phase remains stable for more than 24 h.

GENERAL PROCEDURE

An aqueous phase containing 2.5–250 μg of palladium is transferred to a 125-ml beaker and adjusted to approximately pH 2 using the hydrochloric acid–potassium chloride buffer. The solution is then transferred to a 125-ml separatory funnel, one ml of the saturated solution of 4-methylnioxime is added, and the solution allowed to stand for 1 h. The aqueous phase is then extracted with three 7-ml portions of chloroform. The extracts are combined, transferred to a 25-ml volumetric flask, and diluted to volume with chloroform. As a drying agent, 0.5 g of anhydrous sodium sulfate is added. The absorbance of the chloroform phase is measured against chloroform at 280 mμ using 1-cm silica cells. The amount of palladium is determined by reference to a calibration curve.

INTERFERENCES

The extraction–spectrophotometric method eliminates the interference of many of the highly colored ions which cause trouble in the suspension–spectrophotometric method. However, as in the case of the suspension–spectrophotometric method, the following ions were found to interfere when present: ruthenium(III), copper(II), cobalt(II), iron(II), and iron(III). Successful masking agents were found in all cases except ruthenium. Microgram but not milligram quantities of copper(II) may be masked with thioglycolic acid. Interference from cobalt can be eliminated by conversion to the hexacyanocobaltate(III) complex. Iron(II) can be oxidized to iron(III) and complexed with either tartrate, phosphate, or fluoride; fluoride was found to be the most effective masking agent.

DISCUSSION

One of the outstanding properties of the substituted nioximes is the high solubility in chloroform of the bis (*vic*-dioximato-N,N')metal(II) complexes containing palladium and nickel. Therefore, the quantitative extraction of these complexes into chloroform and a subsequent spectrophotometric determination is possible. 4-Methylnioxime has several advantages over other reagents for the spectrophotometric determination. The pH at which the complex is formed and extracted is not critical, the complex is readily extracted into chloroform, the chloroform solution is stable for more than 24 h, and great sensitivity can be achieved. Interference by highly colored, extractable ions is easily avoided by using readily available masking agents; only ruthenium must be absent when palladium is determined.

The molar absorptivity of the bis(4-methylnioximato-N,N')palladium(II) complex was calculated from the calibration curve and found to be $1.51 . 10^4$ l/moles-cm in chloroform at 280 mμ.

SUMMARY

A procedure for the determination of palladium with 4-methyl-1,2-cyclohexanedionedioxime by an extraction–spectrophotometric method has been developed. Interference by copper(II), cobalt(II), iron(II), or iron(III) can be eliminated by suitable masking agents. Ruthenium(III) must be absent or separated prior to the determination of palladium. The molar absorptivity of the bis(4-methyl-1,2-cyclohexanedionedioximato-N,N') palladium(II) complex has been calculated and found to be $1.51 \cdot 10^4$ l/moles-cm in chloroform at 280 mμ.

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RÉSUMÉ

Une méthode par extraction et par spectrophotométrie est proposée pour le dosage du palladium. On emploie comme réactif la méthyl-4-cyclohexanedionedioxime-1,2.

ZUSAMMENFASSUNG

Es wird eine kombinierte Extraktions-spektrophotometrische Methode zur Bestimmung von Palladium mit Hilfe von Methyl-4-cyclohexandion-dioxim-1,2 beschrieben.

REFERENCES

[1] G. G. Pierson, *Ind. Eng. Chem., Anal. Ed.*, 6 (1934) 437.

[2] G. G. Pierson, *Ind. Eng. Chem., Anal. Ed.*, 11 (1939) 86.

[3] F. Feigl and E. Fränkel, *Ber.*, 65B (1932) 539.

[4] G. H. Ayers and B. L. Tuffly, *Anal. Chem.*, 24 (1952) 949.

[5] I. V. Tananaev, *Zhur. Anal. Khim.*, 3 (1948) 276.

[6] I. V. Tananaev, *Zhur. Anal. Khim.*, 4 (1949) 67.

[7] O. E. Zvyagintzev, *Ann. inst. platine, U.S.S.R.*, (1926) 364.

[8] J. G. Fraser, F. E. Beamish and W. A. E. McBryde, *Anal. Chem.*, 26 (1954) 495.

[9] G. V. Knyazheva, *Izvest. Sektora Platiny i Drug. Blagorod. Metal., Inst. Obshcheĭ i Neorg. Khim., Akad. Nauk S.S.S.R.*, 22 (1948) 129.

[10] E. S. Przheval'skiĭ and V. I. Shlenskaya, *Vestnik Moskov. Univ.*, 7, No. 5, *Ser. Fiz.-Mat. i Estestven. Nauk*, No. 3 (1952) 61.

[11] E. S. Przheval'skiĭ, V. I. Shlenskaya and L. F. Maternykh, *Vestnik Moskov. Univ.*, 9, No. 6, *Ser. Fiz.-Mat. i Estestven. Nauk*, No. 4 (1954) 71.

[12] S. Takaki and Y. Nagase, *J. Pharm. Soc. Japan*, 58 (1938) 324.

[13] F. Feigl, P. Krumholz and E. Rajmann, *Mikrochemie*, 3 (1931) 165.

[14] H. Holzer, *Mikrochemie*, 2 (1930) 271.

[15] L. G. Overholser and J. H. Yoe, *J. Am. Chem. Soc.*, 63 (1941) 3224.

[16] J. H. Yoe and J. J. Kirkland, *Anal. Chem.*, 26 (1954) 1335.

[17] J. H. Yoe and L. G. Overholser, *J. Am. Chem. Soc.*, 61 (1939) 2058.

[18] D. E. Ryan, *Analyst*, 76 (1951) 310.

[19] E. R. Alvarez, *Anales direc. gen. ofic. quím. nacl.* (Buenos Aires), 2 (1949) 88.

[20] K. L. Cheng, *Anal. Chem.*, 26 (1954) 1894.

[21] J. Xavier and P. Rây, *Sci. and Culture (Calcutta)*, 20 (1955) 455.

[22] W. M. MacNevin and O. H. Kriege, *Anal. Chem.*, 26 (1954) 1768.

[23] W. Nielsch, *Mikrochim. Acta* (1954) 532.

[24] M. Ziegler and O. Glemser, *Z. anal. Chem.*, 153 (1956) 246.

[25] V. M. Peshkova, V. I. Shlenskaya and A. I. Rashevskaya, *Vestnik Moskov. Univ.*, 9, No. 5, *Ser. Fiz.-Mat. i Estestven. Nauk*, No. 3 (1954) 83.

[26] V. M. Peshkova, V. I. Shlenskaya and A. I. Rashevskaya, *Izvest. Sektora Platiny i Drug. Blagorod. Metal., Inst. Obshcheĭ i Neorg. Khim., Akad. Nauk S.S.S.R.*, 32 (1955) 61.

[27] E. W. Rice, *Anal. Chem.*, 24 (1952) 1995.

[28] F. E. Beamish and W. A. E. McBryde, *Anal. Chim. Acta*, 9 (1953) 349.

[29] N. C. Sogani and S. C. Bhattacharyya, *Anal. Chem.*, 29 (1957) 397.

[30] A. K. Majumdar and M. M. Chakrabartty, *Anal. Chim. Acta*, 19 (1958) 372.

[31] A. K. Majumdar and M. M. Chakrabartty, *Anal. Chim. Acta*, 19 (1958) 482.

[32] K. Kodama, *Nagoya-shi Kôgyô Kenkyûjo Kenkyû Hôkoku*, 19 (1958) 1.

[33] A. I. Busev and M. I. Ivaniutin, *J. Anal. Chem. U.S.S.R.* (English translation), 13 (1958) 15.

[34] V. M. Peshkova and V. I. Shlenskaya, *Vestnik Moskov. Univ.*, 8, No. 3, *Ser. Fiz.-Mat. i Estestven. Nauk*, No. 2 (1953) 129.

[35] W. Nielsch, *Z. anal. Chem.*, 142 (1954) 30.

[36] O. Menis and T. C. Rains, *Anal. Chem.*, 27 (1955) 1932.

[37] C. V. Banks, D. T. Hooker and J. J. Richard, *J. Org. Chem.*, 21 (1956) 547.

[38] C. V. Banks and D. T. Hooker, *Anal. Chem.*, 28 (1956) 79.

[39] R. C. Voter, C. V. Banks and H. Diehl, *Anal. Chem.*, 20 (1948) 652.

[40] D. T. Hooker, *Ph.D. Thesis*, Iowa State College, 1955.

[41] R. C. Ferguson and C. V. Banks, *Anal. Chem.*, 23 (1951) 448.

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A SYSTEMATIC SCHEME OF QUALITATIVE ANALYSIS FOR CATIONS AND ANIONS

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A procedure has been evolved for the complete analysis of a mixture for its cations and anions. An extensive study of the behaviour of salts of the common elements towards sodium hydroxide and sodium carbonate has led to a procedure which can be used for the simultaneous detection of basic and acid radicals; most of the basic-forming elements when boiled with sodium hydroxide and sodium carbonate behave as acids.

The most important facts which are either already well-known or have come to light are: (a) metals like lead, arsenic, antimony, tin, aluminum and zinc form soluble salts when boiled with sodium hydroxide which are not affected by subsequent treatment with sodium carbonate. (b) Substances like Prussian blue, Turnbull's blue, zinc or copper ferrocyanide, silver ferro- and ferri-cyanides, fused lead chromate, chromium chloride (violet), which are said by some authors to be insoluble in the systematic scheme for basic radicals, are decomposed either with the precipitation of the metal as hydroxide or its conversion to soluble salts, whereas the acid constituent is invariably converted to the soluble sodium salt. (c) Silver, copper, bismuth, cadmium, iron, manganese, nickel and cobalt are completely precipitated as oxides, hydrated oxides or hydroxides. (d) Trivalent chromium salts are converted to $Cr(OH)_3$, which is amphoteric and is partially converted to soluble sodium chromite, which again precipitates $Cr(OH)_3$ on boiling. (e) A fact, which has not hitherto been reported is the behaviour of mercury salts towards sodium hydroxide and sodium carbonate. The precipitation of mercury by sodium hydroxide or sodium carbonate is never complete; mercury is always found in appreciable quantities in the filtrate. (f) The behaviour of the alkaline earths towards sodium hydroxide is already well known. The filtrate obtained after boiling the mixture containing the alkaline earth with sodium hydroxide, contains appreciable amounts of barium and traces of strontium and calcium; the quantity of magnesium depends on the presence of ammonium salts. Unless ammonium salts are completely removed by boiling with a sufficient excess of sodium hydroxide for a fairly long time appreciable amount of magnesium pass into the filtrate. But all the alkaline earths are completely precipitated on further boiling with sodium carbonate. (g) The most important feature of the proposed scheme is the detection of certain metals in the form of anions. These elements are not found in the systematic analysis of the mixture for basic radicals. For example, aluminium and zinc are always converted to their soluble sodium salts, except strongly ignited aluminium oxide, which is treated under insolubles. Lead salts are also completely dissolved by sodium hydroxide, except for lead sulphate which is only partly soluble. Thus provision has to be made for its detection in the scheme for basic radicals, and as an insoluble. Similarly, the sulphides of arsenic, tin and antimony are converted by boiling with sodium hydroxide solution to their soluble thiosalts. However, a very small amount of arsenic and antimony is transformed to the oxides, which are soluble in the subsequent acid treatment for the detection of basic radicals. The behaviour of mercuric sulphide is peculiar; it is partly dissolved on boiling with sodium hydroxide but most of it remains insoluble. This provides a twofold check for the detection of these elements.

In the present work, only a limited number of acid and basic radicals has been selected, *i.e.* those which an elementary student is likely to encounter.

These are:

(*a*) *Acid radicals.* $[Fe(CN)_6]^{-4}$, $[Fe(CN)_6]^{-3}$, F^-, Cl^-, Br^-, I^-, SO_4^{-2}, SO_3^{-2}, S^{-2}, $S_2O_3^{-2}$, CNS^-, PO_4^{-3}, $(COO)_2^{-2}$, CH_3COO^-, NO_3^-, NO_2^-, SiO_3^{-2} and BO_3^{-3}.

(*b*) *Basic radicals.* The so-called common elements which include acid-forming elements like As, Sb, Sn, Pb, Zn, Al etc.

The details of the procedures to be followed in analyzing completely a mixture for its anions and cations are given below.

I. Boil 0.5–1 g of the mixture with 50 ml of 4 *N* sodium hydroxide solution for 4–5 min, add 4–5 g of solid sodium carbonate, boil and filter.

Treat the filtrate for the detection of acid radicals and the residue for basic radicals including the insolubles.

II. Test a portion of the filtrate for lead and treat the rest of the filtrate with lead carbonate (4–5 g), boil and filter. The precipitate may consist of lead carbonate, lead sulphide, mercuric sulphide, mercuric oxide and mercury. Wash with distilled water.

A black precipitate at this stage indicates the presence of sulphide.

Dissolve the precipitate in conc. hydrochloric acid and a crystal of $KClO_3$, boil off chlorine and treat a portion with stannous chloride solution. A white precipitate changing to grey indicates the presence of mercury.

III. Test a portion of the filtrate from II for zinc and treat the rest with 1 *M* zinc acetate solution until no further precipitation takes place, heat to boiling and filter. The precipitate may contain the zinc salts of $[Fe(CN)_6]^{-3}$, $[Fe(CN)_6]^{-4}$, AsO_3^{-3}, AsO_4^{-3}, SO_3^{-2}, $C_2O_4^{-2}$, PO_4^{-3}, $B_4O_7^{-2}$, AlO_2^- and PbO_2^{-2}, but traces of lead and aluminium may also be found in the filtrate. Wash the precipitate with distilled water.

IV. Treat the precipitate from III with an excess of 5 *N* ammonium hydroxide, warm and filter. Wash the insoluble residue with 2 *N* ammonium hydroxide, followed by distilled water and analyse according to Table I.

V. Treat the filtrate from IV with 10 ml of conc. ammonia and add magnesia mixture in slight excess. Heat nearly to boiling and filter. Analyse the precipitate according to Table II.

VI. Treat the filtrate from III with 4–5 g of sodium carbonate, boil and filter. This precipitates Pb^{+2} and Zn^{+2} completely as carbonates and Al^{+3} as hydroxide. (Reject the precipitate). Concentrate the filtrate to 20–30 ml, treat with $Ca(NO_3)_2$ solution in excess and filter. The precipitate consists of $CaCO_3$ and CaF_2.

Test the precipitate for fluoride as usual. Treat the filtrate from CaF_2 with

TABLE I

<table>
<tr><td colspan="3">Ppt. May contain zinc salts of $[Fe(CN)_6]^{-4}$, AlO_2^-, PO_4^{-3}, and PbO_2^{-2}. Boil with 5 <i>N</i> HCl, filter hot and wash with hot water.</td></tr>
<tr><td rowspan="2">Ppt. Zinc ferrocyanide soluble in NaOH. Confirms $[Fe(CN)_6]^{-4}$.</td><td colspan="2">Filt. Chlorides of Zn, Al and Pb, PO_4^{-3}. Add dil. H_2SO_4 in excess and filter. (Reject the ppt. of $PbSO_4$). Treat the filtrate with NH_4Cl and NH_4OH in slight excess and filter.</td></tr>
<tr><td>Ppt. (a) Test a portion for PO_4^{-3} with ammonium molybdate. (b) Test a portion for Al with oxine.</td><td>Filt. Zn^{+2}. Reject.</td></tr>
</table>

TABLE II

<table>
<tr><td colspan="7">Ppt. May contain the magnesium salts of AsO_3^{-3}, AsO_4^{-3}, PO_4^{-3}, (F^-), AlO_2^-, SnO_3^{-2}, SbO_3^{-2} and SbO_4^{-3}. Treat with 4 <i>N</i> acetic acid (15–20 ml) and filter.</td></tr>
<tr><td rowspan="5">Ppt. White $AlPO_4$. Test for Al^{+3} and PO_4^{-3} as usual.</td><td colspan="6">Filt. (F^-), AsO_3^{-3}, AsO_4^{-3}, SbO_3^{-2}, SbO_4^{-3}, SnO_3^{-2}, SiO_3^{-2} and Mg (The presence of Al^{+3} or PO_4^{-3} depends on the amount present in the original mixture). Add $Ca(NO_3)_2$ solution in slight excess and filter.</td></tr>
<tr><td rowspan="4">Ppt. CaF_2. Confirm by SiF_4 test.</td><td colspan="5">Filt. AsO_3^{-3}, AsO_4^{-3}, SbO_4^{-3}, SbO_3^{-2}, SnO_3^{-2}, SiO_3^{-2}, Al^{+3} (Mg+Ca). Add 2 <i>N</i> Na_2S reagent[1] in excess followed by 3–5 g of Na_2CO_3 and filter.</td></tr>
<tr><td rowspan="3">Ppt. PO_4^{-3}, $Al(OH)_3$, $MgCO_3$ and $CaCO_3$. Dissolve in dil. HCl and test for Al^{+3} and PO_4^{-3} as usual.</td><td colspan="4">Filt. Thiosalts of As^{+3}, As^{+5}, Sb^{+3}, Sb^{+5}, Sn^{+4} and Na_2SiO_3(Mg). Make acid with dil. HCl and filter at once.</td></tr>
<tr><td colspan="2">Ppt. As_2S_3, Sb_2S_3, Sb_2S_5 and SnS_2. Boil with 6 <i>N</i> HCl and filter.</td><td colspan="2">Filt. Thiosalts of As^{+5} and Na_2SiO_3. Add conc. HCl to give a final concentration of 6 <i>N</i>, heat to boiling and filter.</td></tr>
<tr><td>Ppt. As_2S_3. Test as usual.</td><td>Filt. Sb^{+3} and Sn^{+4}. Test as usual.</td><td>Ppt. Yellow As_2S_5. Confirms AsO_4^{-3}.</td><td>Filt. SiO_3^{-2}. Evaporate to dryness and dehydrate silica. Test for Si by SiF_4 test.</td></tr>
</table>

$Ba(NO_3)_2$ solution, heat to boiling and filter. Wash the precipitate with distilled water and analyse according to Table III.

TABLE III

<table>
<tr><td colspan="2">Ppt. May contain $BaCrO_4$ and $BaSO_4$. Treat with dil. HCl and filter.</td></tr>
<tr><td>Ppt. $BaSO_4$.
Confirms SO_4^{-2} by carbonized match-stick test.</td><td>Filt. Ba^{+2}, CrO_4^{-2} (HCl). Add NH_4OH in excess. A yellow ppt. confirms CrO_4^{-2}.</td></tr>
</table>

VII. Treat the filtrate from VI with $AgNO_3$ solution in excess, warm to 70° and filter. Test the filtrate for MnO_4^- and the precipitate according to Table IV.

TABLE IV

<table>
<tr><td colspan="4">Ppt. May contain AgCl, AgBr, AgI, AgCNS and Ag_2S.
(A black ppt. of Ag_2S at this stage indicates the presence of thiosulphate). Treat the ppt. with NH_4OH and $(NH_4)_2S$, boil to expel ammonia and filter.</td></tr>
<tr><td rowspan="3">Ppt.
Ag_2S.
Reject.</td><td colspan="3">Filt. CNS^-, I^-, Br^- and Cl^- as ammonium salts. Add HNO_3 and $Fe(NO_3)_3$. Shake with CCl_4 and allow to stand for 5 min.</td></tr>
<tr><td rowspan="2">CCl_4 layer. Purple colour shows I^-.</td><td colspan="2">Aqueous layer. Br^-, Cl^-, $Fe(CNS)_3$ and some iodine. Boil off iodine, cool, dilute and add $KMnO_4$ solution till a light pink colour persists. Shake with CCl_4. ($KMnO_4$ decomposes CNS^-, so that it does not interfere in the tests for Br^- and Cl^-.)</td></tr>
<tr><td>CCl_4 layer. Orange shows Br^-.</td><td>Aqueous layer. Boil off bromine, add $NaNO_2$ and $AgNO_3$. A white ppt. shows Cl^-.</td></tr>
</table>

VIII. Treat the filtrate from V with $Ca(NO_3)_2$ and $Ba(NO_3)_2$, heat to boiling and filter. Analyse the precipitate according to Table V and the filtrate according to Table VI.

IX. Treat the residue from I with 10 ml of conc. HNO_3 and evaporate to nearly 3 ml. Add 20 ml of conc. HCl and evaporate to a moist residue. Boil the residue with 20 ml of 2 *N* HCl and filter.

TABLE V

<table>
<tr><td colspan="4">Ppt. May consist of CaF_2, CaC_2O_4, $BaSO_3$, $BaCrO_4$, BO_3^- and $Ba(OH)_2$. Treat with 5–10 ml of dil. CH_3COOH and filter.</td></tr>
<tr><td colspan="3">Ppt. CaF_2, CaC_2O_4, $BaSO_3$ and $BaCrO_4$. Boil with a saturated solution of Na_2CO_3 for 5 min and filter. Reject the ppt. of $BaCO_3$ and $CaCO_3$. Treat the filtrate with acetic acid in slight excess and add $Ca(NO_3)_2$. Filter.</td><td rowspan="3">Filt. Ba^{+2} and BO_3^-. Evaporate to dryness, take up the residue with dil. HCl and test for borate as usual.</td></tr>
<tr><td rowspan="2">Ppt. CaF_2, CaC_2O_4.
Confirm F^- and $C_2O_4^{-2}$ as usual.</td><td colspan="2">Filt. SO_3^-, CrO_4^{-2} (Ca). Add bromine-water followed by HCl and $BaCl_2$.</td></tr>
<tr><td>Ppt. $BaSO_4$
Confirms SO_3^{-2}.</td><td>Filt. CrO_4^{-2}, Ba and HCl. Add NH_4OH in excess. A yellow ppt. confirms CrO_4^{-2}.</td></tr>
</table>

(A) The insoluble residue may contain halides: AgCl, CaF_2; sulphates: $BaSO_4$, $SrSO_4$, $Cr_2(SO_4)_3$ (anhydrous), $PbSO_4$; strongly ignited oxides: SiO_2, Sb_2O_4, SnO_2, Al_2O_3, Cr_2O_3 and $Sn_2P_2O_7$. Analyse as usual[2].

(*Note*: The treatment of the residue with $4N$ sodium hydroxide solution may be omitted here.)

TABLE VI

Filt. May contain $[Fe(CN)_6]^{-3}$, BO_3^{-3}, and traces of Sb and Sn (Ba+Ca). Add NH_4OH in slight excess, followed by 2–4 g of Na_2CO_3. Boil for 5 min and filter.	
Ppt. $BaCO_3$ and $CaCO_3$. Reject.	Filt. $[Fe(CN)_6]^{-3}$, BO_3^{-3} and traces of Sb and Sn. Divide in two parts. *Part I*. Acidify with dil. HCl and test for $[Fe(CN)_6]^{-3}$ with $FeSO_4$ solution. Blue ppt. or colour confirms $[Fe(CN)_6]^{-3}$. *Part II*. Evaporate to dryness and test for borate by BF_3 test. Note: The solution need not be tested for Sn and Sb here; these elements have already been tested for in Table II.

(B) The filtrate may be tested for the following elements according to the scheme based on the decomposition of thiosalts[3]: Hg, (Pb), Bi, Cu, Cd, Ni, Co, Mn, Fe, Cr, (As), (Sb), (Sn) and alkaline earths. The elements shown in brackets are present in very small amounts.

X. *Detection of S^{-2}*. Certain sulphides are not decomposed on boiling with alkali as suggested in I. A separate portion of the original mixture must be tested for this anion.

Detection of NH_4^+. Heat a portion of the original mixture with sodium hydroxide and test for ammonia.

Detection of Na^+ and K^+. Extract a portion of the original mixture with 10–15 ml of distilled water, treat with concentrated ammonium sulphide and filter. From the filtrate remove the metals of the arsenic and tin groups by decomposing the thiosalts and filter off the precipitated sulphides. Test the filtrate for Mg^{+2}, Na^+ and K^+ as usual.

SUMMARY

The behaviour of different elements towards sodium hydroxide and sodium carbonate is reviewed. Detailed procedures for the complete analysis of a mixture containing anions and cations are given.

RÉSUMÉ

L'auteur a examiné le comportement de différents éléments vis-à-vis de l'hydroxyde et du carbonate de sodium. Une méthode d'analyse complète anions et cations est décrite.

ZUSAMMENFASSUNG

Es wurde das Verhalten verschiedener Elemente gegen Natriumhydroxyd und Natriumcarbonat untersucht und ein vollständiger Trennungsgang der Anionen und Kationen beschrieben.

REFERENCES

[1] I. K. Taimni and G. B. S. Salaria, *Anal. Chim. Acta*, 13 (1955) 28.
[2] G. B. S. Salaria, *Anal. Chim. Acta*, 13 (1955) 513.
[3] G. B. S. Salaria, *Anal. Chim. Acta*, 14 (1956) 97; 19 (1958) 605.

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THE USE OF CONTINUOUS EXTRACTION FOR THE REMOVAL OF INTERFERING ELEMENTS IN THE DETERMINATION OF CALCIUM AND MAGNESIUM

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Many elements interfere in the determination of calcium and magnesium by titration with ethanediaminotetraacetic acid (VERSENE). The interference of some of these elements can be reduced by combining them with reagents such as cyanide, 2,3-dimercaptopropanol[1], and triethanolamine[2-5], which form very strongly bound complexes with them. Although methods using complexing agents are satisfactory when small amounts of interfering elements are present, the end-points of the titrations of calcium and magnesium are not so sharp if large amounts of such elements are present.

Certain of the interfering elements can be removed by precipitation with ammonium hydroxide, but others, such as copper and nickel, which form soluble ammines, remain in the solution. This method of separation is rather tedious, since, owing to the coprecipitation of calcium and magnesium, one or two reprecipitations are necessary to free the precipitate of alkali earth metals. With organic precipitants, such as 8-hydroxyquinoline (oxine), the risk of co-precipitation is reduced, but some calcium and magnesium are still carried down by the precipitate. Methods of separation employing solvent extraction are often more satisfactory than those using precipitation, since co-extraction of elements does not usually occur. ESKELUND AND BROWN[6] have extracted iron as its diethyldithiocarbamate with ether before the titration of calcium and magnesium. CLULEY[7] has described a procedure for the determination of calcium in soda–lime glasses, in which iron and aluminium are separated by extraction of their oxinates at pH 5.0 with chloroform.

The author[8,9] has used a similar method in silicate analysis for the removal of iron, aluminium and titanium before titration of calcium and magnesium. The extraction was carried out at pH 5 using a continuous extractor instead of a separating funnel. This had the following advantages:
a. less manipulation was required; b. excess oxine was rapidly removed; c. emulsions, which formed in the presence of much iron, when a separating funnel was used, were avoided.

Since many other elements which interfere in the determination of calcium and magnesium also form oxinates which are soluble in chloroform, it was expected that this method could be used in the analysis of silicate minerals and other materials, containing large amounts of such elements. This paper describes an investigation into the removal of such elements with a continuous extractor. Phosphate, arsenate and selenate, when present in major amounts, seriously interfere in the determination of calcium and magnesium.They can be removed by precipitation as their insoluble zirconium salts; excess zirconium is removed as its oxinate during the extraction process.

Titration of calcium and magnesium

The use of Eriochrome Black T (E.B.T.) as an indicator in the titration of total calcium + magnesium in ammoniacal medium with ethanediaminotetraacetic acid, is well known and gives satisfactory end-points, either visually or with a photoelectric titrator.

The titration of calcium in the presence of an equal, or larger amount of magnesium is more difficult, and a number of indicators such as murexide, calcein[10–13], Eriochrome Blue Black R (Calcon)[14,15], and Calred[16], have been used for the purpose. Before the titration, the solution is made alkaline to precipitate magnesium as its hydroxide, which does not titrate. Some calcium is co-precipitated with the magnesium hydroxide, but this can be removed by vigorous stirring during the titration. The co-precipitation of calcium can be minimized by precipitating the magnesium hydroxide at a lower pH using a diethylamine buffer[15] or by the addition of sucrose to the solution[17].

An intercomparison of the four above mentioned indicators for the titration of calcium, in the presence of considerable amounts of magnesium, was made as described in the experimental section. It was found (Table I) that Calcon was a very satisfactory indicator for work with *ca.* 1–2 mg of calcium, particularly if the end-point was detected photoelectrically. Calcein when used as a fluorescent indicator in screened ultra-violet radiation, gave a very sharp end-point which was much sharper than the normal visual end-point obtained with this indicator.

TABLE I

DETERMINATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM USING CALCEIN AND CALCON AS INDICATORS

Calcein used fluorimetrically		*Calcon used with photometric end-point*	
mg MgO present	*(wt. of CaO taken 5.00 mg) mg CaO found*	*mg MgO present*	*(wt. of CaO taken 1.00 mg) mg CaO found*
10	4·98 4·99 5·01	1	0.999
30	4·98 4·97 4·99	3	0.996
50	4·97 4·94	6	0.992

EXPERIMENTAL

An "Eel" photoelectric titrator was used for all titrations with Eriochrome Black T and Calcon indicators.

Reagents

For separation of interfering elements: Zirconium nitrate 2% w/v. Dissolve 2 g of "Specpure" zirconium nitrate in 100 ml of 1 *N* nitric acid. Filter the solution through a fine textured filter paper.

8-Hydroxyquinoline reagent. Prepare a 20% w/v solution of 8-hydroxyquinoline in acetone.
Acetylacetone.
Sodium acetate 2 *M*. Dissolve 272 g of sodium acetate trihydrate in water and dilute to 1 l.
Chloroform B.P.,
Sodium chlorite (85%),
Acetic acid 0.2 *N*.

For titration of calcium + magnesium: Ethanediaminotetraacetic acid (VERSENE). Prepare a solution containing 2.50 g of the disodium salt of ethanediaminotetraacetic acid and 0.1 g of hydrated magnesium chloride in 2 l of water. Add *ca.* 2 ml of chloroform to prevent the growth of moulds.

Ammonium hydroxide–ammonium chloride buffer. Dissolve 70 g of ammonium chloride in 600 ml of ammonium hydroxide ($d = 0.880$) and dilute to 1 l with water.

Eriochrome Black T indicator (E.B.T.). Prepare a solution containing 0.2% w/v of the solid indicator in ethyl alcohol.

For titration of calcium, using Calcein as indicator: Ethanediaminotetraacetic acid (VERSENE). Add 1 ml of calcein indicator to 2 l of VERSENE reagent prepared as described above.

Sodium hydroxide 10% w/v. Store in a polyethylene bottle.

Calcein indicator. Dissolve 1 g of Calcein[10] in 12.5 ml of *N* sodium hydroxide and dilute to 50 ml.

Using Calcon as indicator: Ethanediaminotetraacetic acid (VERSENE). Dilute 125 ml of VERSENE reagent to 1 l.
Diethylamine.
Calcon indicator. Dissolve 0.1 g of powdered Calcon[14] in 25 ml of methyl alcohol. Prepare as required.
Standard solutions: Magnesium solution. Dissolve 0.3015 g of "Specpure" magnesium in a slight excess of dilute hydrochloric acid, dilute to 1 l. 1 ml of this solution is equivalent to 0.5 mg of MgO.

Calcium solution: Dissolve 0.8925 g of calcium carbonate (dried at 110°) in a slight excess of hydrochloric acid. Dilute to 1 l. 1 ml of this solution is equivalent to 0.5 mg of CaO.

PROCEDURE

Removal of interfering elements in the absence of manganese, phosphate, arsenate and selenate

The continuous extractor used for the removal of interfering elements is that described in an earlier communication[8]. Place about 250 ml of chloroform in the 500-ml flask attached to the extractor and 50–75 ml of chloroform in the body of the extractor.

Pipette a suitable aliquot of the solution to be analysed (containing up to 50 mg each of CaO and MgO, and having an acidity of not more than 0.2 *N*) into a 500-ml conical flask, and add water to a total volume of *ca.* 200 ml. Add, with shaking, 10 ml of the solution of 8-hydroxyquinoline in acetone and 20 ml of 2 *M* sodium acetate. The pH of the solution should now be 4.9–5.2; if it is less than this, add more sodium acetate solution. If lead, molybdenum, uranium or zirconium are present, filter the solution through a Buchner funnel using a hardened filter paper (Whatman No. 52); wash the precipitate with water and add the washings to the filtrate. If cerium, chromium or beryllium are present add 5 ml of acetyl acetone and warm to 100° for 30 min under reflux.

Extract the cold solution with chloroform in the continuous extractor for 30 min, when it should be completely clear and colourless. Any coloured droplets adhering to the walls of the extractor are of no consequence since they are removed later. Pour the liquid in the extractor into a 500-ml separating funnel, rinse the extractor well with water and add the rinsings to the separating funnel. Run off the lower layer. Filter the aqueous layer through a Whatman No. 1 filter, and collect the filtrate in a 500-ml graduated flask. Wash the separating funnel and filter paper and make the solution up to volume.

Removal of manganese

Manganese is not extracted by 8-hydroxyquinoline in chloroform at pH 8 and remains with calcium and magnesium in the extracted solution. It can be quantitatively precipitated from this solution by boiling with sodium chlorite. Boil the extracted solution (not diluted to volume) for 10 min to remove dissolved chloroform. Cool for a few min and then add *ca.* 0.3 g of sodium chlorite and boil until the precipitated manganese dioxide has coagulated. Allow the precipitate to settle for a short time and then decant the supernatant liquid through a Whatman No. 1 filter. Wash the precipitate once with 50 ml of water and twice with 30-ml portions of 0.2 *N* acetic acid to remove adsorbed calcium and magnesium. Combine the filtrate and washings and add 10% hydroxyammonium chloride dropwise until the yellow colour caused by oxides of chlorine is discharged. When cold, dilute to 500 ml.

Removal of phosphate, arsenate and selenate

Dilute the sample solution to *ca.* 150 ml and make it *ca.* 0.1 *N* in hydrochloric acid. Heat it almost to boiling and add a macerated 5.5-cm ashless filter paper and 25 ml of 2% zirconium nitrate solution. Boil for 5 min and filter through a hardened filter paper using suction. Wash the precipitate thoroughly with hot 0.05 *N* hydrochloric acid. Combine the filtrate and washings, cool, and add 10 ml of 8-hydroxyquinoline and 50 ml of 2 *M* sodium acetate solution. Filter off the precipitate, which consists principally of zirconium quinolinolate, using a hardened paper with suction. Wash the precipitate with 20–30 ml of water. Add a further 10 ml of 8-hydroxyquinoline reagent to the filtrate and extract it as described above.

Titration of magnesium + calcium

Place 12.5 ml of the extracted solution ($\not>$ 7.5 mg of Ca + Mg) in the 60-ml beaker of a photoelectric titrator, add 5 ml of ammonium hydroxide buffer and 0.5 ml of the E.B.T. indicator. Titrate the solution with VERSENE solution using a microburette and a photoelectric titrator with a filter having maximum transmission at 600 mμ (Ilford No. 607). If the titration is performed visually, 50 ml of the extracted solution should be taken and the amounts of buffer and indicator doubled. The end-point of the titration occurs when the solution becomes a pure blue green colour free from all traces of pink.

Titration of calcium

Using Calcein. Pipette 100 ml of the extracted solution ($\not>$ 5 mg CaO) into a porcelain basin. Add 10 ml of 10% sodium hydroxide, stir vigorously for 1 min and then add 0.06 ml of Calcein indicator. Titrate the solution in screened ultra-violet light with VERSENE reagent containing calcein. The approach of the end-point is indicated by a change in the fluorescence of the solution from bright yellow to dark brown. Continue the addition of VERSENE reagent, dropwise, with stirring after the addition of each drop, until no brown colour is formed where the drop enters the solution.

Using Calcon. Pipette 12.5 ml of the extracted solution into a 60-ml beaker of the photoelectric titrator. Add 1 ml of the standard magnesium solution (0.25 mg MgO/ml) and 4 ml of diethylamine to bring the solution to about pH 12.3. Stir the solution vigorously for 3 min with a magnetic stirrer to complete the precipitation of magnesium hydroxide. Add 0.5 ml of Calcon* indicator, and titrate the solution with dilute VERSENE solution on the photoelectric titrator, using a filter having its maximum transmission at 600 mμ (Ilford No. 607). If the titration is performed visually, it is continued until all traces of pink have disappeared and the solution has become a pure blue green colour.

Standardization of VERSENE *solutions*

During the extraction, a small amount of the aqueous phase (less than 1%) becomes entrained or dissolved in the chloroform; it is therefore necessary to standardize the VERSENE solutions with extracted calcium and magnesium solutions. Carry out extractions, as described above, on distilled water, to which 50 ml of standard calcium solution have been added, and on distilled water containing 50 ml of standard magnesium solution. Titrate 12.5 ml aliquots of the extracted calcium and magnesium solutions with VERSENE reagent, using E.B.T. as indicator. If the titration of calcium is carried out using Calcein indicator, titrate 100-ml portions of the extracted standard calcium solution; if it is performed photometrically using Calcon, titrate 12.5-ml portions of the extracted standard solution. Normally, the reagent blanks for the method are negligible, but they should be determined by extracting distilled water, as described above, with each fresh batch of reagents.

RESULTS

In order to test the proposed method, mixtures of known amounts of metals (known to interfere in the VERSENE titration) with the equivalent of 25 mg each of calcium and magnesium oxides were extracted as described above. The extracted solutions were then titrated to determine calcium and magnesium remaining. The results (Table II) show that in most cases removal of the interfering element was complete and satisfactory recoveries of calcium and magnesium were obtained. Some elements, such as cerium, beryllium and chromium were not extracted as their 8-hydroxyquinoline complexes but were readily extracted after chelation with acetylacetone[18].

Manganese is not extracted at all by 8-hydroxyquinoline in chloroform at pH 5.0, and is not completely removed by extraction with acetylacetone. It is readily precipitated quantitatively at pH 5 as the hydrated dioxide by boiling the extracted solution with sodium chlorite. Provided that the precipitate is filtered as soon as it has coagulated, only small amounts of calcium and magnesium are co-precipitated, and these may be removed by washing the precipitate with dilute acetic acid. Determination of 20 mg each of CaO and MgO in the presence of 50 and 100 mg of manganese gave recoveries of CaO + MgO of 99.6% and 99.4% respectively after removal of manganese as the dioxide. Small amounts of manganese can be tolerated in the VERSENE titrations. No correction is necessary for its presence in the titration of calcium using Calcein as indicator; manganese can be titrated with VERSENE reagent in ammoniacal solution using E.B.T., provided that a reducing agent such as ascorbic acid is present.

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* In preliminary work, both murexide and Calred were tested as indicators under these conditions, but were found to be less sensitive than Calcon, if much magnesium was present.

TABLE II

REMOVAL OF INTERFERING ELEMENTS BEFORE TITRATION OF CALCIUM AND MAGNESIUM

Element	*Wt. (mg)*	*CaO found (mg)*		*MgO found (mg)*	
Aluminium	200	24.98	25.03	24.96	25.07
Beryllium[a]	100	24.84	25.05	24.85	25.12
Bismuth	200	24.90	—	25.10	—
Cadmium	100	25.03	25.02	25.10	25.07
Cerium[a] (Ce^{+3})	50	24.89	24.77	25.20	25.25
Chromium[a] (Cr^{+3})	100	25.00	25.03	25.00	24.90
Cobalt	100	24.93	24.86	25.12	25.16
Copper	100	24.94	24.92	25.14	25.15
Gallium	100	25.04	24.94	24.92	24.95
Indium	100	25.03	25.05	25.10	25.10
Iron (Fe^{+3})	100	25.03	24.97	24.96	25.03
Lanthanum[c]	100	25.34	25.24	27.14	26.94
Lead[b]	100	24.96	24.82	25.04	25.12
Manganese	5	24.90	24.90	—	—
Mercury (Hg^{+2})	100	24.89	24.90	25.20	25.25
Molybdenum[b] (Mo^{+6})	100	25.01	25.06	24.92	24.97
Nickel	200	24.95	—	24.97	—
Thallium (Tl^{+})	100	25.00	25.00	25.00	25.06
Thorium	100	24.94	24.88	24.85	24.80
Tin (Sn^{+2})	200	25.10	24.95	25.04	25.04
Titanium (Ti^{+4})	10	25.00	24.96	24.92	24.93
Tungsten[b] (W^{+6})	100	24.91	24.94	24.91	24.95
Uranium (UO$_2^{+2}$)	100	24.94	24.92	25.04	25.08
Vanadium[a] (V^{+5})	100	25.16	25.20	25.13	25.23
Zinc	200	24.93	—	25.15	—
Zirconium (Zr^{+4})	200	24.97	25.08	25.13	25.11

[a] Precipitate of oxinate filtered off, 5 ml of acetylacetone added.
[b] Oxinate precipitate filtered off before extraction.
[c] Not completely extracted even when 5 ml of acetylacetone was used.

Lanthanum and the rare earths are not extracted by 8-hydroxyquinoline and chloroform at pH 5.0, but it is very probable that they could be extracted at a pH of *ca.* 8.0. Their extraction by acetylacetone was not investigated.

Although small amounts of phosphate, arsenate and selenate are without effect on the titration of calcium and magnesium with VERSENE reagent, their presence in large amounts leads to low results owing to the formation of stable calcium and magnesium complexes. These interfering anions are readily removed by precipitation

TABLE III

REMOVAL OF INTERFERING ANIONS FROM CALCIUM AND MAGNESIUM

Anion	*Wt. of element*	*CaO recovered (mg)*		*MgO recovered (mg)*	
Arsenate	100 mg As	24.87	25.10	25.07	24.89
Phosphate	100 mg P	25.03	25.06	25.13	24.87
Selenate	100 mg Se	25.11	24.89	25.05	24.95

in acid solution as their insoluble zirconium salts; excess of zirconium is easily removed as its oxinate during the extraction process. Table III shows the excellent recoveries of calcium and magnesium obtained from solutions, originally containing the equivalent of 25 mg each of CaO and MgO, when interfering anions had been precipitated as their zirconium salts.

SUMMARY

Solvent extraction with a continuous extractor has been used to separate Al, Be, Bi, Cd, Ce, Cr, Co, Cu, Ga, In, Fe, Pb, Hg, Mo, Ni, Tl, Th, Sn, Ti, W, U, V, Zn and Zr, from calcium and magnesium, before titration of the latter with ethanediaminotetraacetic acid. Most of these elements are extracted at *ca.* pH 5.0 as their chelates with 8-hydroxyquinoline using chloroform. Be, Ce and Cr are not extracted under these conditions and are converted into their acetylacetonates, before extraction with chloroform. Manganese is not quantitatively removed by any of these processes and is precipitated as its hydrated dioxide by boiling the extracted solution with sodium chlorite. Phosphate, arsenate and selenate can be removed by precipitating them in acid solution with excess zirconium nitrate, and removing the latter with 8-hydroxyquinoline.

RÉSUMÉ

L'auteur propose une séparation du calcium et du magnésium d'avec de nombreux ions (Al, Bi, Cd, Ce, Cr, Co, Cu, Ga, Gl, In, Fe, Pb, Hg, Mo, Ni, Tl, Th, Sn, Ti, W, U, V, Zn et Zr) en effectuant une extraction par solvant au moyen d'un extracteur continu. Le calcium et le magnésium peuvent être finalement titrés par l'acide éthylènediaminotétracétique.

ZUSAMMENFASSUNG

Calcium und Magnesium können von vielen anderen Ionen (Al, Bi, Cd, Ce, Cr, Co, Cu, Ga, Gl, In, Fe, Pb, Hg, Mo, Ni, Tl, Th, Sn, Ti, W, U, V, Zn und Zr) nach einem kontinuierlichen Extraktionsverfahren mit Hilfe eines Lösungsmittels abgetrennt und dann durch Titration mit Aethylendiaminotetraessigsäure bestimmt werden.

REFERENCES

[1] R. Pribil and Z. Roubal, *Chem. listy*, 48 (1954) 818.
[2] R. Pribil and Z. Roubal, *Collection Czechoslov. Chem. Communs.*, 19 (1954) 1162.
[3] R. Pribil, *Chem. listy*, 47 (1953) 1333.
[4] W. Nielsch, *Glas-Email-Kergmo-Tech.*, 6 (1955) 73.
[5] O. Podlaha and J. Ullman, *Ceskoslov. hyg. epidemiol. mikobiol. imunol.*, 4 (1955) 260.
[6] G. R. Eskelund and F. E. Brown, *Proc. Louisiana Acad. Sci.*, 18 (1955) 105.
[7] H. J. Cluley, *Analyst*, 54 (1954) 567.
[8] J. P. Riley, *Anal. Chim. Acta*, 19 (1958) 413.
[9] J. P. Riley and H. P. Williams, *Mikrochim. Acta*, (in the press).
[10] H. Diehl and J. L. Ellingboe, *Anal. Chem.*, 28 (1956) 882.
[11] G. Schwarzenbach and R. Salman, *U.S. Patent*, 2,745,720 (1956).
[12] S. J. Socolar and J. I. Salach, *Anal. Chem.*, 31 (1959) 473.
[13] A. J. Barnard, W. C. Broad, H. Flaschka, *Chemist Analyst*, 46 (1957) 18.
[14] G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, 31 (1948) 1029.
[15] G. P. Hildebrand and C. N. Reilly, *Anal. Chem.*, 29 (1957) 258.
[16] J. Patton and W. Reeder, *Anal. Chem.*, 28 (1956) 1026.
[17] B. M. Tucker, *Analyst*, 82 (1957) 284.
[18] G. H. Morrison, and H. Freiser, *Solvent Extraction in Analytical Chemistry*, John Wiley and Sons, New York 1957, pp. 157–9.

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SPECTROPHOTOMETRIC DETERMINATION OF IRON WITH QUINOLINIC ACID

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Quinolinic acid as a reagent for the gravimetric and volumetric estimation of palladium has already been described[1]. Quinolinic acid, like picolinic and quinaldinic acids[2], forms with ferrous iron a soluble yellow complex, which at pH 5.9 exhibits maximum absorption at 420 mμ. On the addition of potassium cyanide, however, the colour changes to orange yellow and the region of maximum absorption to 440 mμ. The latter colour reaction is specific for ferrous iron and a thorough study of quinolinic acid as a spectrophotometric reagent for iron has been made. The complex obeys Beer's law at 440 mμ with ferrous ion concentrations of 1 to 16 p.p.m., the optimum range being 4–16 p.p.m. with a relative error of 2.94% per 1% absolute photometric error. The molar extinction coefficient of the complex at 440 mμ is 2946.

EXPERIMENTAL

Apparatus and solutions

Spectrophotometric measurements in 1-cm quartz cells were made with a Hilger Uvispeck spectrophotometer. Corrections were made, when necessary, to compensate for slight differences in the transmittancies of the cells.

Iron solution

Standard iron solution was prepared by dissolving a known amount of ferric nitrate (A.R., B.D.H.) in 100 ml of water containing 5 ml of conc. A.R. nitric acid. The solution was boiled to oxidize any ferrous iron, cooled and made up to 1 l. The iron content was determined gravimetrically (1.727 mg of iron per ml). Weaker solutions were prepared by proper dilution.

Reagent solution

Quinolinic acid[3] was prepared by the oxidation of 8-hydroxy-quinoline with fuming nitric acid. The reagent was crystallized first from 40% acetic acid, and then several times from water. A 1% aqueous solution of the reagent, m.p. 192–194°, was prepared for spectrophotometric study.

Other solutions

A 0.15 *M* (approx. 1%) solution of potassium cyanide (standardized by silver nitrate solution) and a 1% solution of hydroxylamine hydrochloride were used.

Solutions of diverse ions were prepared from their reagent grade, iron-free chemicals and the amount present per ml of each solution was determined by standard methods.

Colour reaction and maximum absorption

Aliquots of standard iron solutions were taken in 25-ml flasks. To each flask, 1 ml of the hydroxylamine hydrochloride solution, 6 ml of the reagent solution, 10 ml of the potassium cyanide solution and a few ml of water to make up the volume were added. The orange–yellow complex formed instantaneously on the addition of cyanide showed maximum absorption at 440 mμ. At room temperature, it was highly stable and maintained its transmittancy for 12 h. Curve I (Fig. 1) shows the absorption of the reagent against water, while curves II and III represent that of the complex corresponding to 8 p.p.m. of iron against water and reagent respectively as blanks.

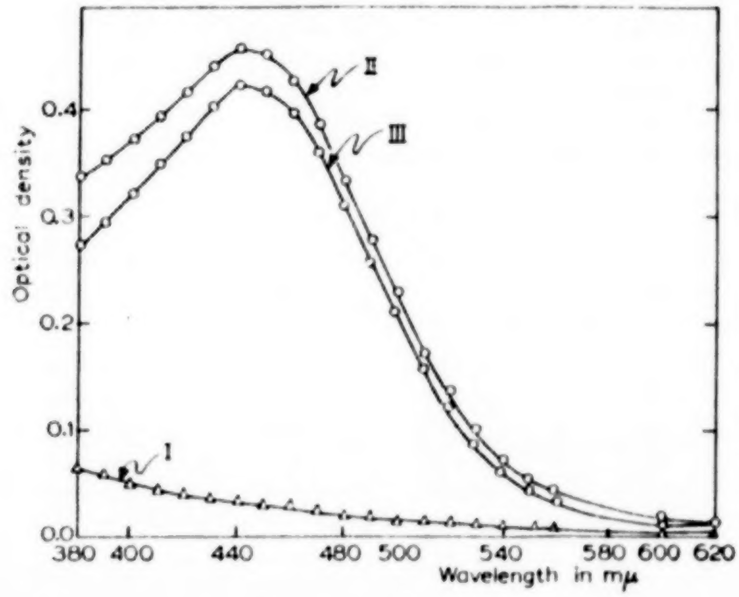

Fig. 1. Spectral transmittancy curve. Curve I: absorption of reagent against water as blank. Curve II: absorption of the complex corresponding to 8 p.p.m. of iron against water as blank. Curve III: absorption of the above complex against reagent as blank.

Effect of the reagent, cyanide and the reducing agent

The effects of quinolinic acid, potassium cyanide and hydroxylamine hydrochloride were studied at 440 mμ; the amount of one reagent was varied while the concentrations of the other two were kept constant. For the maximum colour development, the respective amounts of the reagent, cyanide and hydroxylamine hydrochloride were about 250, 250 and 50 times that of the ferrous iron (Table I).

Effect of pH

The pH's of 1% solutions of quinolinic acid, and its mono- and disodium salts are respectively 2.1, 3.6 and 6.5. Under the experimental conditions, the pH of the coloured

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complex formed by ferrous quinolinate with potassium cyanide is 9.0, but without potassium cyanide (ferrous: reagent as 1:2) the pH must be maintained between 5.4 and 6.5 (Table II).

TABLE I

Iron 8 p.p.m., reagent 5 ml, cyanide 5 ml, hydroxylamine hydrochloride 1 ml

Reagent ml	*O.D.*	*Cyanide ml*	*O.D.*	*Hydroxylamine hydrochloride ml*	*O.D.*
1	0.381	1	0.103	0.25	0.381
2	0.399	2	0.152	0.5	0.418
3	0.411	3	0.211	1.0	0.422
4	0.420	4	0.415	1.25	0.422
5	0.422	5	0.422		
6	0.422	6	0.422		

TABLE II

pH	*O.D.*	*pH*	*O.D.*
1.5	0.031	6.0	0.164
2.2	0.062	6.5	0.164
3.0	0.074	7.0	0.150
4.0	0.089	8.0	0.143
5.0	0.160	9.0	0.132
5.4	0.164		

Beer's law and optimum range

To verify Beer's law, the optical densities of the solutions prepared from 1–40 p.p.m. of iron were measured at 440 mμ against a reagent blank. Fig. 2, representing the optical density – concentration curve, shows that Beer's law is obeyed up to 16 p.p.m. of iron.

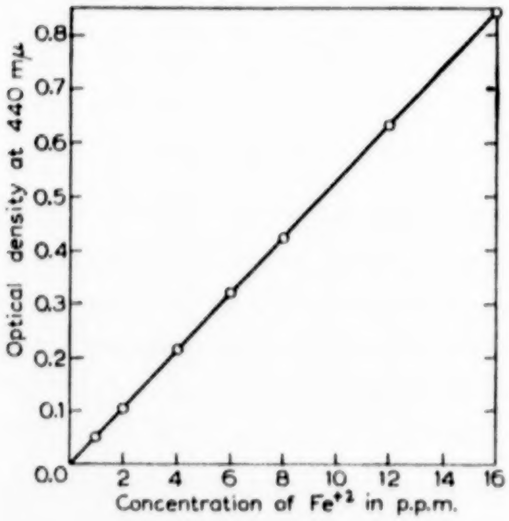

Fig. 2. Beer's law for the iron complex.

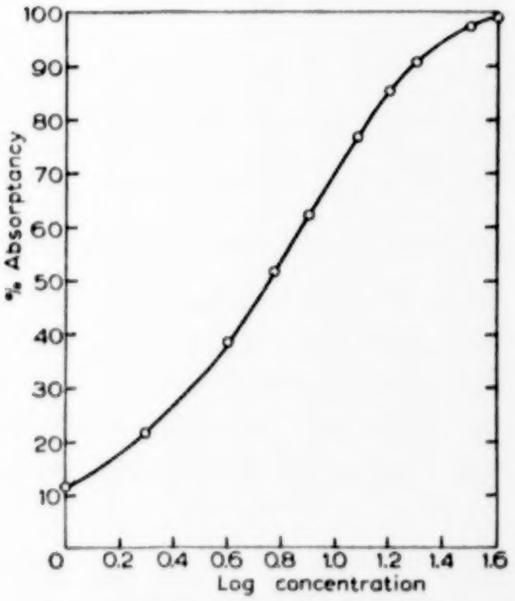

Fig. 3. Calibration curve for the iron complex.

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In order to define a suitable concentration range and to evaluate the accuracy in photometric analysis, the % absorbance as ordinate was plotted against the log of concentration as abscissa, as proposed by RINGBOM[4]. The accuracy is greatest at the steepest slope of the curve (Fig. 3), and the optimum concentration range, is 4–16 p.p.m. In this range, the relative error per 1% absolute photometric error is readily obtained by AYRES method[5] as 2.94% from the following equation:

$$\frac{\%\ \text{relative analysis error}}{1\%\ \text{absolute photometer error}} = \frac{230}{\dfrac{\mathrm{d}I}{\mathrm{d}\log C}}$$

where I and C have their usual significance.

Influence of foreign ions

The effect of ions was studied by measuring the colour intensity of the iron complex from 8 p.p.m. of iron in presence of the ion. An ion was considered to interfere if it caused a difference of 0.005 unit in optical density from that of the original complex. (*cf.* Table III).

TABLE III

Ion	*Added as*	*Limiting concentration p.p.m.*
Cd^{+2}	$Cd(NO_3)_2$	100
Pb^{+2}	$Pb(NO_3)_2$	150
Hg^{+2}	$HgCl_2$	60
Al^{+3}	$Al(NO_3)_3$	150
Zn^{+2}	$Zn(NO_3)_2$	70
Mn^{+2}	$MnCl_2$	80
Co^{+2}	$Co(NO_3)_2$	40
Ni^{+2}	$Ni(NO_3)_2$	50
Ca^{+2}	$CaCl_2$	100
Ba^{+2}	$BaCl_2$	80
Sr^{+2}	$Sr(NO_3)_2$	75
Mg^{+2}	$MgCl_2$	100
Th^{+4}	$Th(NO_3)_4$	150
Ti^{+4}	$Ti(SO_4)_2$	30
UO_2^{+2}	$UO_2(NO_3)_2$	200

The alkali metals, silver, chloride, iodide, nitrate, sulphate, acetate, tartrate, vanadate and molybdate have no effect on the colour system. In some cases, an excess of the cyanide solution was needed to maintain the required alkalinity or to dissolve the precipitate formed.

Composition and dissociation of the complex

The empirical formula of the complex in solution was determined by Job's method of continuous variation[6], and by the molar-ratio[7] and slope-ratio[8] methods.

Job's method: For the evaluation of the composition of the complex formed in presence of potassium cyanide, the iron content was varied from 1 to 9 ml of the $2.66 \cdot 10^{-3}$ *M* solution. The photometric data are shown graphically in Fig. 4. The maximum point in the graph indicates that in solution the iron and the reagent are in a ratio of 1:1. In the absence of potassium cyanide, the complex formed at pH 5.9 (buffered with sodium acetate and acetic acid) shows a maximum absorption at 420 mμ and this complex as determined by the above procedure with $5 \cdot 10^{-3}M$ iron solution has a 1:2 ratio of iron to reagent.

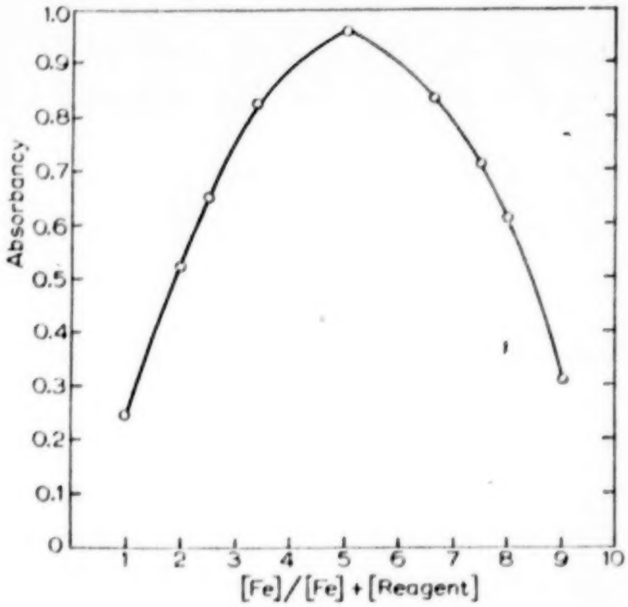

Fig. 4. Determination of the ratio of iron(II) to reagent by Job's method.

Molar ratio method: With equimolar solutions ($5.32 \cdot 10^{-3}$ *M*) of the reagent and iron, the ratio of iron to reagent was varied from 1 : 0.2 to 1 : 1.6 and the optical densi-

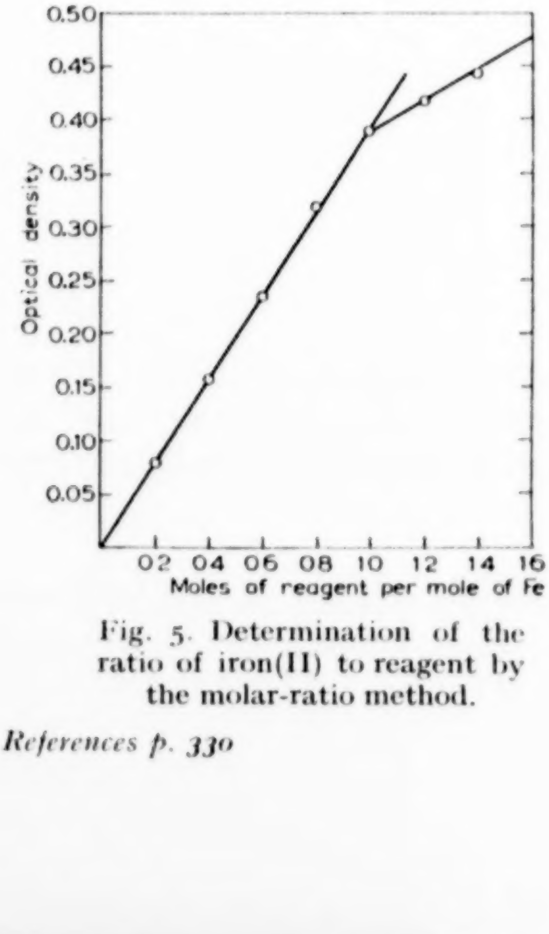

Fig. 5. Determination of the ratio of iron(II) to reagent by the molar-ratio method.

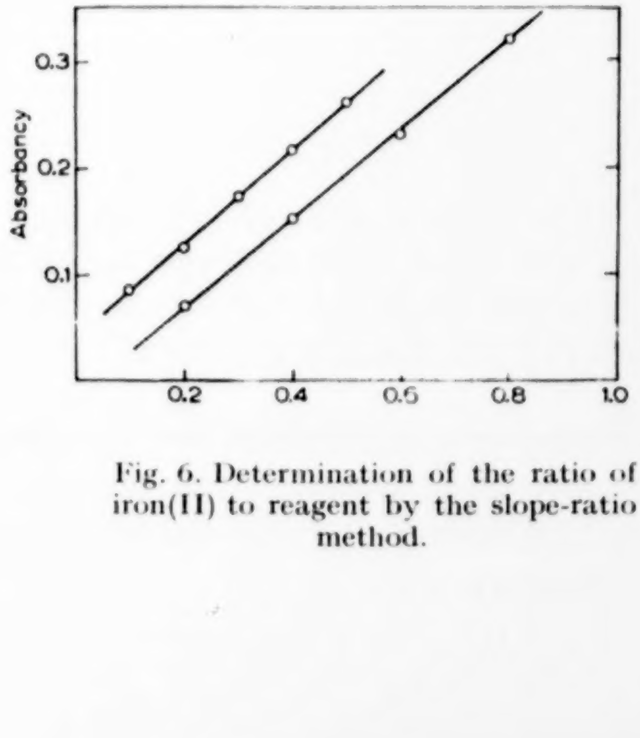

Fig. 6. Determination of the ratio of iron(II) to reagent by the slope-ratio method.

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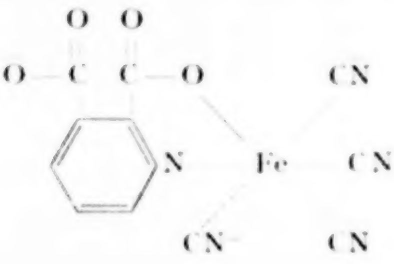
ties of the solutions prepared with hydroxylamine hydrochloride and potassium cyanide were measured at 440 mμ. The curve (Fig. 5) obtained shows a break at a ratio of 1 mole of reagent to 1 mole of iron. But the coloured product formed at pH 5.9 in the absence of cyanide gave a break at an iron to reagent ratio of 1:2.

Slope ratio method: This method helped to confirm the composition. Two series of solutions were used. In one series varying amounts of $5.32 \cdot 10^{-4}\,M$ reagent solution were added to a constant amount of iron solution (1 ml of $5.32 \cdot 10^{-3}\,M$), while in the other series, the iron solution ($5.32 \cdot 10^{-4}\,M$) was varied and the reagent solution was kept constant (4 ml of $5.32 \cdot 10^{-3}\,M$). All transmittancy measurements were made at 440 mμ (Fig. 6). The ratio of the slopes of the two straight lines confirms that the complex formed in presence of potassium cyanide contains the metal and the reagent in a ratio of 1:1. The composition of the complex without potassium cyanide could not be ascertained by this method, because the large excess of reagent added changes the nature of the complex and shifts the region of maximum absorption to 440 mμ.

Thus the formulae of the 1 : 1 and 1 : 2 complexes may be suggested as $K_4[Fe(C_7H_3NO_4)(CN)_4]$ and $Na_2[Fe(C_7H_3NO_4)_2(H_2O)_2]$ and represented respectively as



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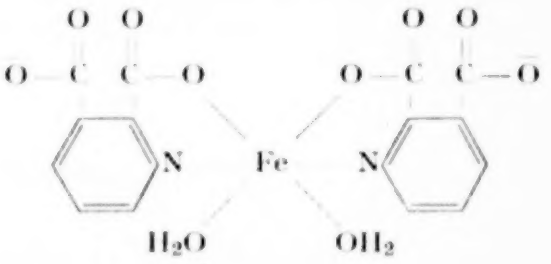

Dissociation

The degree of dissociation, α, and the instability constant, K, were calculated according to the equations of HARVEY AND MANNING[8]. The degree of dissociation, $\alpha = (E_m - E_s)/E_m$, where E_m is the absorption at 440 mμ due to a given amount of the metal ion completely complexed with an excess of the reagent and E_s is the absorbance calculated for the same amount of the metal ion complexed with a stoichiometric amount of the reagent.

The values for E_m and E_s being 0.422 and 0.260 for the complex with cyanide, α equals 0.384; without cyanide, E_m and E_s are 0.162 and 0.085 respectively and α equals 0.478.

The instability constant, K, of the complex is obtained by substituting the value of α in the equation $K = \alpha C(n\alpha C)^n/C(1-\alpha)$, where C is the concentration of the metal ion in moles per l and n is the number of moles of the reagent required for complex formation with 1 mole of the metal ion. Thus for the complex with cyanide, $K = 2.73 \cdot 10^{-5}$ and for the complex without cyanide, $K = 1.72 \cdot 10^{-9}$.

SUMMARY

Quinolinic acid forms two complexes with ferrous ion. One is formed at pH 5.9 and has maximum absorption at 420 mμ; the metal to reagent ratio is 1:2 and the instability constant is about $1.7 \cdot 10^{-9}$. The other complex is formed with an excess of potassium cyanide and shows maximum absorption at 440 mμ; the metal to reagent ratio is 1:1; the instability constant is only $2.73 \cdot 10^{-5}$. The latter complex adheres to Beer's law from 1 to 16 p.p.m. of iron, and its optimum concentration range is 4–16 p.p.m. of iron, where the percent relative error per 1% absolute photometric error is only 2.94.

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The reagent is highly specific and can be used spectrophotometrically for the determination of very small quantities of iron in presence of many cations.

RÉSUMÉ

L'acide quinoléique est proposé pour le dosage spectrophotométrique du fer(II). Ce réactif, en présence de cyanure de potassium, permet le dosage de très petites quantités de fer, à côté d'un grand nombre de cations étrangers.

ZUSAMMENFASSUNG

Sehr kleine Mengen Eisen(II) lassen sich neben einer ganzen Anzahl von Fremdionen spektrophotometrisch mit Hilfe von Chinolinsäure in Gegenwart von Kaliumcyanid bestimmen.

REFERENCES

[1] A. K. MAJUMDAR AND S. P. BAG, *Z. anal. Chem.*, 165 (1959) 247.
[2] A. K. MAJUMDAR AND B. SEN, *J. Indian Chem. Soc.*, 27 (1950) 245; *Anal. Chim. Acta*, 8 (1953) 369.
[3] E. SUCHARDA, *Ber.*, 58B (1925) 1727-29.
[4] A. RINGBOM, *Z. anal. Chem.*, 115 (1938) 332
[5] G. H. AYRES, *Anal. Chem.*, 21 (1949) 652.
[6] P. JOB, *Compt. rend.*, 180 (1925) 928; *Anal. Chim., Paris*, [10] 9 (1928) 113.
[7] J. H. YOE AND A. L. JONES, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 111.
[8] A. E. HARVEY, JR., AND D. L. MANNING, *J. Am. Chem. Soc.*, 72 (1950) 4488; 74 (1952) 4744.

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SEPARATION OF NIOBIUM AND TANTALUM WITH PHENYLARSONIC ACID

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Phenylarsonic acid has been used as reagent for the separation and estimation of zirconium, thorium[1], tin[2] and bismuth[3] in presence of other interfering elements. FUCKE AND DAUBLANDER[4] attempted the separation of niobium and tantalum in a sulphuric acid–hydrogen peroxide solution, whereas DUPRAW[5] used *n*-propyl-arsonic acid for the separation in a sulphuric acid–oxalic acid solution.

In the present work, no precipitate of niobium or tantalum could be obtained with phenylarsonic acid from a sulphuric acid-hydrogen peroxide solution. However, tantalum was precipitated completely from oxalate solutions of acidities varying from 10% (v/v) sulphuric acid up to pH 5.8; but the precipitation of niobium was complete only when the pH exceeded 4.8. Much ammonium oxalate tended to keep both the niobium and tantalum in solution; not more than 25 times the amount of the oxides of niobium or tantalum should be present. Thus from a mixed solution tantalum was precipitated at a pH below 3.0 or preferably from a 5% (v/v) sulphuric acid solution, and niobium was recovered from the filtrate after adjusting the pH to 5.0 with ammonium acetate. When the concentration of ammonium oxalate in the filtrate exceeded the above limit, cupferron was found suitable for the recovery. This method worked well with ratios of Ta_2O_5 to Nb_2O_5 greater than 1 : 2. But when the $Nb_2O_5 : Ta_2O_5$ ratio was more than 2.0, dissolution and reprecipitation of the tantalum was necessary to free it from the co-precipitated niobium, and even then the results were not very accurate.

With complexone III as the masking agent, tantalum could be separated at pH 2.0–3.0 from numerous ions, except titanium, zirconium, lead, barium and strontium. In presence of an excess of stannous, thorium and uranyl ions, a double precipitation of tantalum was needed to obtain the pure oxide.

As phenylarsonic acid failed to precipitate niobium in presence of complexone III, its separation from other ions was attempted by the cupferron method as suggested by MAJUMDAR and RAY CHOWDHURY[6]. But the claim of the authors that niobium, in presence of complexone III, can be separated from iron, aluminium, chromium, zirconium, thorium, and antimony at a pH 4.5 to 5.5 could not be confirmed; for those ions remained in solution only at a high pH of about 7.0, where the precipitate due to niobium became colloidal. However, at pH 4.5 to 5.5 complexone III masks, in presence of cupferron, the influence of the ions of zinc, manganese, nickel, cobalt, arsenic, copper, cadmium, bismuth, mercury, calcium, magnesium, vanadate, molybdate, tungstate, chromate and arsenate.

EXPERIMENTAL

Reagents, solutions and apparatus

Chemicals and their solutions used were the same as reported previously[7]. Phenylarsonic acid was prepared according to the method of PALMER AND ADAMS[8]; a 5% aqueous solution was used as the precipitant. The wash solution was made by dissolving 0.5 g of the reagent and 1 g of ammonium nitrate in 100 ml of warm water.

Standard solutions of niobium and tantalum were prepared from their pentoxides (specpure, Johnson, Matthey & Co.). A weighed quantity was fused with potassium bisulphate (G. R. E. Merck) and extracted with an ammonium oxalate solution of a particular strength and diluted with water to a definite volume. The niobium or tantalum content of the solution thus obtained was determined from an aliquot portion of the solution by the cupferron method[9].

A Cambridge pH meter was used for all pH measurements.

Effect of complexing agents

From a tartrate solution maintained at any acidity between 10% (v/v) sulphuric acid and pH 1.6, both niobium and tantalum are precipitated, but when the pH is increased to over 3.0, both dissolve. From an ammonium oxalate solution, however, they are precipitated at different acidities or pH regions; the presence of ammonium oxalate in excess of 25 times the amount of the tantalum or niobium oxide keeps the oxide concerned in solution. Although the tantalum precipitate has no definite composition, it contains on average about 2 moles of the reagent per gram atom of tantalum. About 0.5 g of the reagent per every 10 mg of the pentoxide is required for complete precipitation.

Effect of pH

An aliquot of the standard solution of niobium or tantalum was mixed with sufficient ammonium oxalate solution to keep its concentration between 20 and 25 times the amount of oxide present, the solution was diluted to 150 ml and its pH was adjusted either with dilute sulphuric acid or with ammonium acetate solution. An excess of the reagent solution was then added to the boiling hot solution and the boiling continued for 2–5 min. The precipitate was filtered, washed with the wash solution (to prevent its becoming colloidal), dried, ignited to oxide in a muffle furnace and weighed. The region of complete precipitation for tantalum was from an acidity of 10% (v/v) sulphuric acid to a maximum pH of about 5.8. For niobium, precipitation began at pH 4.0 and was complete when the pH was raised to above 4.8.

TABLE I

Ta_2O_5 taken mg	*Nb_2O_5 taken mg*	*Ta_2O_5 found mg*	*Nb_2O_5 found mg*
8.4	12.2	8.6[a]	12.0[a]
16.8	18.3	16.4[a]	18.0[a]
8.4	24.4	8.6[b]	24.0[b]
8.4	183.0	8.0[c]	182.2[c]
20.2	5.5	20.6[a]	5.0[a]
93.2	14.8	93.6[a]	15.0[a]
186.4	14.8	186.8[a]	14.6[a]

[a] single precipitation.
[b] double precipitation.
[c] triple precipitation.

Separation of niobium and tantalum

After the addition of ammonium oxalate, about 25 times the quantity of tantalum pentoxide present, to the solution containing both niobium and tantalum, the acidity was adjusted to 5% (v/v) with respect to sulphuric acid and the tantalum was precipitated, washed, ignited and weighed as above. The filtrate and washings of the tanta-

TABLE II

Ta_2O_5 taken mg	*Ions added*	*mg*	*Ta_2O_5 found mg*	*Ta_2O_5 taken mg*	*Ions added*	*mg*	*Ta_2O_5 found mg*
20.2	Fe^{+3}	240.0	20.2	20.2	Sn^{+2}	108.0	20.6
20.2	Cr^{+3}	100.0		20.2	Cu^{+2}	100.0	
	Al^{+3}	100.0			Cd^{+2}	100.0	20.2
	R.E.	100.0	20.6		Bi^{+3}	100.0	
	Ce^{+4}	100.0			Hg^{+2}	100.0	
	Be^{+2}	60.0					
				20.2	Zn^{+2}	100.0	
20.2	UO_2^{+2}	120.0	20.0				
					Mn^{+2}	100.0	20.2
20.2	Th^{+4}	120.0	20.4		Ni^{+2}	100.0	
					Co^{+2}	100.0	
20.2	Ca^{+2}	100.0		18.4	As^{+3}	100.0	18.4
	Mg^{+2}	100.0	20.2		Sb^{+3}	100.0	
9.2	PO_4^{-3}	100.0	9.6	9.2	WO_4^{-2}	125.0	9.6
9.2	CrO_4^{-2}	120.0	9.2	9.2	MoO_4^{-2}	130.0	9.4
9.2	VO_3^{-}	100.0	9.2				

R.E. = Rare Earths.

lum precipitate were mixed and heated to boiling, and niobium was precipitated after raising the pH to 5.0 by neutralisation. However, if the ammonium oxalate concentration of this solution was higher than the stated limit, as was usually the case when the amount of niobium pentoxide was less than in the 1 : 1 ratio of Ta_2O_5 : Nb_2O_5, niobium was recovered in the cold by cupferron. When the above ratio was lower than 1 : 2, that is when the niobium content was very high, reprecipitation of tantalum was necessary for complete separation. Results are given in Table I.

Separation of tantalum from other ions

After the addition of an excess of complexone III to mask interfering ions, tantalum was precipitated at pH 2–3 according to the above procedure. Tantalum was thus separated from all the ions except those of titanium, zirconium, lead, barium and strontium. The presence of a large excess of stannous, thorium and uranyl ions required a second precipitation. Results are given in Table II.

SUMMARY

Phenylarsonic acid permits satisfactory separation of niobium and tantalum and estimation of tantalum from an oxalate solution containing sulphuric acid up to pH 5.8. For complete precipitation of niobium the pH should exceed 4.8. In mixtures, tantalum is precipitated below pH 3.0 and niobium is then precipitated above pH 5.0. When the oxalate concentration is high, recovery of niobium with cupferron is recommended. When the ratio of Nb_2O_5 to Ta_2O_5 exceeds 2 : 1, reprecipitation of tantalum is necessary. The effect of interfering ions is studied.

RÉSUMÉ

L'acide phénylarsonique est proposé comme réactif pour la séparation du niobium et du tantale, en solution oxalique. L'auteur a étudié les conditions de précipitation et l'influence des agents complexants. En présence de fortes concentrations d'oxalate, on recommande le dosage du niobium au moyen de cupferron.

ZUSAMMENFASSUNG

Es wird die Trennung von Niob und Tantal in oxalathaltiger Lösung mit Hilfe von Phenylarsinsäure beschrieben. Die Fällungsbedingungen und der Einfluss anderer Kationen in Gegenwart von Komplexon III wurden untersucht. In Gegenwart von viel Oxalat wird die Fällung des Niobs mit Kupferron empfohlen.

REFERENCES

[1] A. C. Rice, H. C. Fogg and C. James, *J. Am. Chem. Soc.*, 48 (1926) 895.
[2] J. S. Knapper, K. A. Craig and G. C. Chandlee, *J. Am. Chem. Soc.*, 55 (1933) 3945.
[3] A. K. Majumdar, *J. Indian Chem. Soc.*, 21 (1944) 119, 187, 188; 22 (1945) 313.
[4] H. Fucke and J. Daublander, *Tech. Mitt. Krupp A. Forschungsber.*, 2 (1939) 174; *C.A.*, 34 (1940) 40.
[5] W. A. Dupraw, *Anal. Chem.*, 27 (1955) 309.
[6] A. K. Majumdar and J. B. Ray Chowdhury, *Anal. Chim. Acta*, 19 (1958) 18.
[7] A. K. Majumdar and A. K. Mukherjee, *Anal. Chim. Acta*, 19 (1958) 23.
[8] C. S. Palmer and R. Adams, *J. Am. Chem. Soc.*, 44 (1922) 1361.
[9] H. Pied, *Compt. rend.*, 15 (1923) 1071.

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STUDIES IN THE SPECTROPHOTOMETRIC DETERMINATION OF SILICON IN MATERIALS DECOMPOSED BY HYDROFLUORIC ACID

I. LOSS OF SILICON BY DECOMPOSITION WITH HYDROFLUORIC ACID

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INTRODUCTION

Most of the proposed methods for the photometric determination of silicon are based on the formation of yellow silicomolybdic acid or its reduction product, molybdenum blue. Yellow silicomolybdic acid is formed in acid solution by reaction between silicate ions and molybdate ions. Silicon in materials not decomposed by the acids normally applied is converted to acid soluble silicates by fusion or heating with an alkali. By acidification small amounts of hydrated silica remain in solution.

Hydrofluoric acid is not usually applied for the decomposition of samples in which silicon is determined, because of the fear of losing silicon as the volatile silicon tetrafluoride. A survey of the extensive literature on the spectrophotometric determination of silicon shows only a limited number of procedures in which hydrofluoric acid is used as decomposing agent. In these cases hydrofluoric acid is applied in combination with other acids. It has not been possible to find procedures in which hydrofluoric acid is used as the sole decomposing agent.

CASE[1] used hydrofluoric acid in addition to the usual acids to increase the rate of dissolution of certain nonferrous alloys in which silicon was finally determined photometrically as yellow silicomolybdic acid. CASE made the important observation that a given amount of silicon, whether it is present as fluosilicic acid or as hydrated silica, gives the same extinction when measured photometrically as the yellow silicomolybdic acid. CASE used boric acid to complex the excess of hydrofluoric acid.

An important discovery concerning the spectrophotometric determination of silicon was made by STRICKLAND[2], who found that yellow silicomolybdic acid exists in two modifications, one of which is an unstable β-acid which is more or less rapidly converted to the stable α-acid. The extinctions of the two modifications are different at the wavelengths usually applied for photometric measurement. This discovery explains the many contradictory data given in earlier publications on the yellow silicomolybdic acid. Recent publications[3,4] recommend that the stable α-silicomolybdic acid be used for analytical purposes.

The present series of papers describes experiments in which silicon-containing materials are decomposed by hydrofluoric acid and the content of silicon is determined spectrophotometrically.

The present paper describes series of experiments in which known amounts of silica are decomposed by excess hydrofluoric acid.

In one series of experiments the content of silica (present as fluosilicic acid) is determined spectrophotometrically as α-silicomolybdic acid immediately after dissolution. The resulting extinction data are compared with those obtained from another, corresponding series of solutions of α-silicomolybdic acid prepared from standard solutions of hydrated silica. Solutions of hydrated silica are prepared by the conventional decomposition of silica with sodium carbonate.

In another series of experiments solutions of fluosilicic acid in hydrofluoric acid are evaporated at different temperatures. The amounts of silica remaining in solution are then determined at different stages of evaporation.

EXPERIMENTAL

Instruments

Extinction measurements were made at 20° ± 1° C with a Zeiss spectrophotometer PMQ II. Matched sets of 1,000-cm silica and glass cells were used.

For the measurement of pH a Beckman pH-Meter model H-2 (glass and calomel electrodes) was used.

Reagents

Spectrographically standardized silicon dioxide (Johnson, Matthey & Co.) was used for the experiments. This product left no residue when volatilised by evaporation with hydrofluoric acid.

Reagent grade hydrofluoric acid (35–40%) always contains some fluosilicic acid. The content of the latter was determined (by the procedure to be described in paper No 2 of this series) in the hydrofluoric acid used (E. Merck) and corrections were made for the amounts present.

Other chemicals were of reagent grade quality with the exception of aluminium chloride hexahydrate which was of pharmaceutical grade. Ordinary distilled water was used.

The pH was adjusted with solutions of hydrochloric acid and ammonia.

Apparatus

The experiments on evaporation at temperatures above room temperature were carried out in teflon beakers (50 mm outer, 47 mm inner diameter, height 50 mm, capacity about 100 ml) made from compact teflon rod. The beakers fitted closely into cylindrical aluminium blocks (75 mm outer, 50 mm inner diameter) placed on an electrically heated magnetic stirrer, the temperature being regulated with a Sunvic energy regulator. A teflon-covered magnet was used for stirring.

The temperature of the hydrofluoric acid solutions was measured with a special sensitive thermocouple, one branch consisting of 70% gold and 30% palladium, the other of 90% platinum and 10% rhodium. The thermocouple was standardized against a standard mercury thermometer. The unisolated end of the thermocouple dipped into the solution to be measured.

For experiments at room temperature ordinary plastic beakers (capacity about 300 ml) were used.

A special pipette made from thin-walled teflon tube (inner diameter about 2 mm) was constructed for sampling solutions containing hydrofluoric acid. The teflon tube was placed inside a glass tube and extended about 2 cm at the lower end. A rubber suction bulb fitted on to the upper end. The pipette was calibrated to contain 1 ml.

Basic chemical equilibria

When silica is dissolved in excess hydrofluoric acid the ternary system $HF-H_2SiF_6-H_2O$ is formed; this system was investigated by MUNTER, AEPLI, AND KOSSATZ[5], who found a constant-boiling ternary solution of composition 10% hydrofluoric acid, 36% fluosilicic acid and 54% water (boiling point 116.1° at 759.7 mm pressure).

The azeotropic mixture of $HF-H_2O$ was found by the same authors to have a composition of 38.26% HF (boiling point 112.0° at 750.2 mm pressure).

The liquid–vapour equilibria diagram of the system $HF-H_2SiF_6-H_2O$ shows that a liquid mixture of the three components which has a composition in the vicinity of constant-boiling hydrofluoric acid, is in equilibrium with a vapour mixture in which the concentration of fluosilicic acid is considerably lower than in the liquid.

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This fact makes it possible to decompose silicon-bearing samples of hydrofluoric acid without losing any, or only negligible amounts of, silicon by evaporation.

Loss of silicon by the decomposition of silica with hydrofluoric acid

A series of experiments was carried out in which weighed amounts of silica were dissolved in known amounts of 35–40% hydrofluoric acid. The amounts of silicon remaining in solution were determined spectrophotometrically as yellow α-silicomolybdic acid. Time, temperature and volumes of hydrofluoric acid were varied in these experiments.

For the photometric determination of silicon in the different solutions, a calibration curve was needed and was prepared by fusing 1.0000 g of silicon dioxide with 10.0 g of sodium carbonate. The melt was dissolved in diluted hydrochloric acid, and the solution was transferred to a 1-l volumetric flask and made up to the mark. This solution contained 1 mg of SiO_2 per ml and was stored in a plastic bottle. Varying amounts of this standard solution were pipetted into 300-ml plastic beakers containing about 50 ml of water, 10 ml of 10% ammonium molybdate solution were added, the pH was adjusted to 1.0 ± 0.5, and the silicomolybdic acid was converted to the stable α-acid by heating the solutions for 3 h on a boiling water bath (watch glass). The solutions were then cooled to room temperature, transferred to 100-ml volumetric flasks and diluted to the mark. The extinction of the series of solutions was measured at 415 mμ against a blank containing all the reagents and prepared in exactly the same way.

The extinction data at 415 mμ showed that Beer-Lambert's law is followed up to at least 10 mg of SiO_2 per 100 ml.

Another calibration curve was prepared by dissolving (in a 300-ml plastic beaker) 100.0 mg of silicon dioxide (moistened with 2–3 drops of water to avoid a violent reaction) in 5 ml of hydrofluoric acid (35–40%). The silicon dioxide, which was in a very reactive form, dissolved rapidly without heating. To the solution were added 200 ml of 25% aluminium chloride solution. After being transferred to a 500-ml volumetric flask the solution was diluted to the mark with distilled water. This standard solution contained 0.2 mg of SiO_2 per ml.

From this solution different volumes were pipetted into a series of 300-ml plastic beakers, 10 ml of 10% ammonium molybdate were added and the solutions were diluted to about 90 ml. With the pH-meter, the pH was adjusted to 1.0 ± 0.5, and the beakers were placed on the boiling water bath for 3 h. These solutions were then treated and their extinctions measured as above.

Table I gives the extinction data for the two series of solutions of α-silicomolybdic acid prepared from silicic acid and from fluosilicic acid.

When the usual errors of photometric determinations are considered, the two curves can be said to be identical. Consequently, no silicon seems to be lost by evaporation when silica is decomposed by hydrofluoric acid. The data in Table I also confirm the observation made by CASE that the extinction of α-silicomolybdic acid is the same whether silicon is present as silicate or as fluosilicate ions.

It now remained to determine the loss of silicon from solutions evaporated at room or a higher temperature.

In plastic or teflon beakers weighed amounts of silica (about 50 mg) were dissolved

TABLE I

EXTINCTION AND EXTINCTION INDEX (E/C) FOR SOLUTIONS OF α-SILICOMOLYBDIC ACID PREPARED FROM SILICIC AND FLUOSILICIC ACID. WAVE-LENGTH 415 mμ, 1.000-cm CELLS

Mg SiO_2 per 100 ml	*Extinction and extinction index of solutions of α-silicomolybdic acid*			
	Prep. from silicic acid		*Prep. from fluosilicic acid*	
	Extinction	*Extinction index*	*Extinction*	*Extinction index*
1.0	0.100	0.100	0.099	0.099
2.0	0.194	0.097	0.193	0.097
3.0	0.296	0.099	0.294	0.098
4.0	0.388	0.097	0.388	0.097
5.0	0.482	0.096	0.480	0.096
6.0	0.578	0.096	0.575	0.096
7.0	0.683	0.098	0.680	0.097
8.0	0.781	0.098	0.779	0.097
9.0	0.878	0.098	0.880	0.098
10.0	0.980	0.098	0.979	0.098
		0.977		0.973

in weighed amounts of hydrofluoric acid (35–40%). The fluosilicic acid originating from the hydrofluoric acid was included in the amounts of silicon dissolved.

The silica was weighed into the beaker and moistened with 2 drops of water. Hydrofluoric acid was weighed in a small plastic beaker with a tightly fitting plastic stopper. The acid was then added to the silica which rapidly dissolved.

The series of beakers to be kept at room temperature was placed in a hood, precautions being taken to avoid contamination by dust. Beakers to be heated were prepared and placed singly in the aluminium block and stirring and heating was started. After 5–10 min the prefixed temperature was reached and then maintained. After a suitable amount of acid had evaporated, the beaker was removed and rapidly cooled to room temperature in ice water. The beaker (teflon or plastic) was weighed (equipped with a plastic stopper) and the remaining amount of solution was calculated. When the residue weighed less than 1 g, it was transferred quantitatively to a plastic

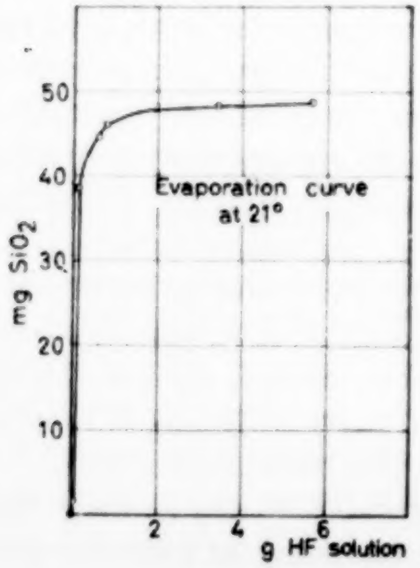

Fig. 1

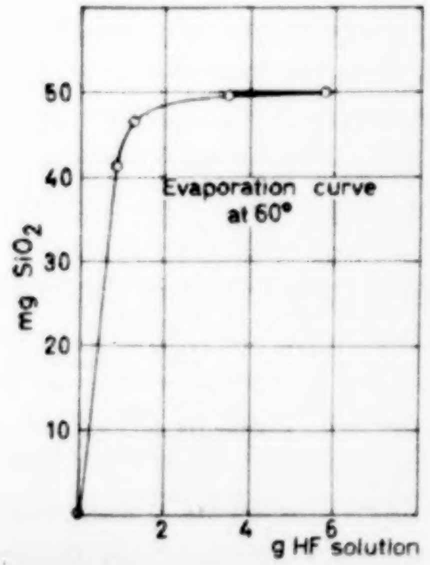

Fig. 2

beaker (300 ml) containing 50 ml of 25% aluminium chloride solution and 10 ml of 10% ammonium molybdate solution. The mixture was diluted to about 90 ml with water, the pH was adjusted and the solution heated and diluted as described above. Finally, the extinction was measured at 415 mμ against a blank containing ammonium molybdate and aluminium chloride and adjusted to pH 1.0 ± 0.5. The amount of silica remaining was then calculated.

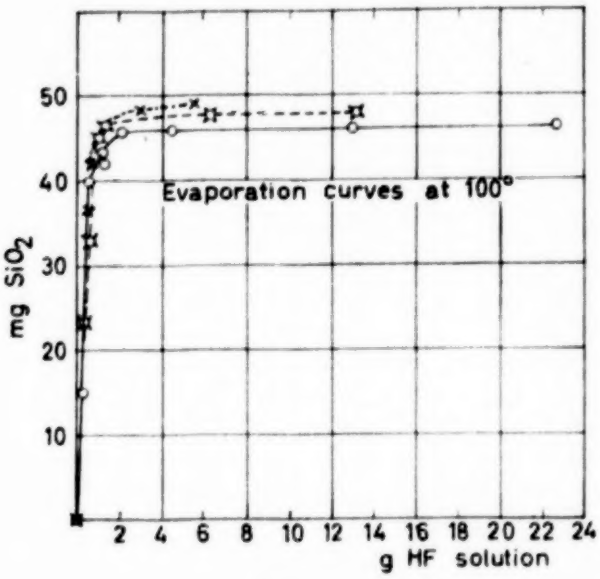

Fig. 3.

When the remaining solution weighed more than 1 g, about 1 ml was pipetted out (with the teflon tube pipette) into a plastic beaker and the solution was reweighed. The further treatment was as described above.

Experiments were carried out at room temperature (21° ± 2°) and at 60° ± 2° and at 100° ± 2°. The volumes of hydrofluoric acid used were normally about 5 ml; for the experiments at 100°, 10 and 20 ml were also used.

Solutions of about 5 ml, maintained at room temperature and at 100°, were evaporated to dryness in the course of about 110 h and 30 min, respectively. In Figs. 1, 2 and 3 the curves giving the loss of silicon by evaporation are reproduced.

CONCLUSION

It can be concluded that silica is decomposed by excess of hydrofluoric acid without any detectable loss of silicon through evaporation. It is interesting to note that this decomposition can also be carried out safely at higher temperatures, *e.g.* 100°.

When solutions of fluosilicic acid in hydrofluoric acid are evaporated by standing at room temperature or higher temperatures, only small amounts of silicon are lost initially; this is evident from the horizontal part of the evaporation curves. The break in these curves indicates that the composition of the constant-boiling ternary mixture of hydrofluoric acid, fluosilicic acid and water is reached. This ternary mixture then evaporates undecomposed, as indicated by the nearly vertical part of the curves. The concentration of fluosilicic acid in these final ternary solutions is roughly the same as given by MUNTER, AEPLI AND KOSSATZ[5] for this mixture, *i.e.* 36%.

Finally, it may be mentioned that solutions evaporated to dryness, *e.g.* at room temperature, contain only traces of silicon. In one experiment at room temperature the residue contained 0.1 mg SiO_2, corresponding to 0.2% of the original amount.

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SUMMARY

Hydrofluoric acid can be used to dissolve silicon-containing materials without loss of silicon by evaporation. Silicon (present as fluosilicic acid) can then be determined spectrophotometrically as the yellow *α*-silicomolybdic acid. The loss of silicon from solutions evaporated at room temperature and higher temperatures is also determined.

RÉSUMÉ

Les substances renfermant du silicium peuvent être dissoutes dans l'acide fluorhydrique, sans risque de perte de cet élément par évaporation. Après dissolution, le silicium (sous forme d'acide fluosilicique) peut être dosé par spectrophotométrie, comme acide *α*-silicomolybdique jaune.

ZUSAMMENFASSUNG

Siliziumhaltige Substanzen können in Fluorwasserstoffsäure gelöst werden ohne Gefahr eines Verlustes an Silizium durch Verdunstung. Das in der Lösung als Silikofluorwasserstoffsäure vorliegende Silizium kann durch Überführung in die gelbe *α*-Silikomolybdänsäure spektrophotometrisch bestimmt werden.

REFERENCES

[1] O. P. CASE, *Anal. Chem.*, 16 (1944) 309.
[2] J. D. H. STRICKLAND, *J. Am. Chem. Soc.*, 74 (1952) 862.
[3] L. H. ANDERSSON, *Acta Chem. Scand.*, 12 (1958) 495.
[4] A. RINGBOM, P. E. AHLERS AND S. SIITONEN, *Anal. Chim. Acta*, 20 (1959) 78.
[5] P. A. MUNTER, O. T. AEPLI AND RUTH A. KOSSATZ, *Ind. Eng. Chem.*, 39 (1947) 427.

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A NEW INDICATOR FOR THE COMPLEXOMETRIC DETERMINATION OF CALCIUM

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INTRODUCTION

Glyoxal bis-(2-hydroxy-anil) was first described by BAYER[1] as a complex-former for different metal ions. Later it was found that this anil in alkaline solution forms a red salt with calcium ions which permits a specific and sensitive identification of the cation[2].

The red calcium salt is destroyed by an aqueous solution of ethylenediaminetetraacetic acid (EDTA), hence the indicator properties of glyoxal bis-(2-hydroxy-anil) in the complexometric titration of calcium were examined.

EXPERIMENTAL

Reagents

1. Glyoxalbis (2-hydroxy-anil), 0.02% ethanolic solution. The compound was obtained as described by BAYER[1,2]. 2. Calcium chloride. A stock solution containing 0.5 g Ca/l was prepared by dissolving calcium carbonate in the minimum amount of hydrochloric acid. From this more diluted solutions were prepared. 3. EDTA (disodium salt). Approximately 0.01 *M* aqueous solution. This was standardized against the calcium chloride solution by using either Eriochrome Black T or the new indicator. In both cases the same results were obtained. 4. Potassium cyanide. 0.5% aqueous solution. 5. 1 *N* sodium hydroxide.

PROCEDURE

To 100 ml of the test solution add 10 ml of 1 *N* sodium hydroxide, 1 ml of potassium cyanide solution and 10 ml of the indicator solution. Stir until a red or pink colour appears. Titrate with EDTA to a pure yellow.

Table I shows typical results obtained.

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DISCUSSION

The end-point of the titration is indicated by a sharp change from pink to yellow.

The ethanolic solution of the indicator is colourless. If stored in a dark bottle and refrigerated it remains almost colourless for at least three months. If kept in a clear bottle, the solution turns yellow after a few days, but may still be used for at least a month. Because of the insolubility of glyoxal bis-(2-hydroxy-anil) in water, the results were better with 10 ml of an ethanolic solution than with a smaller volume of a more concentrated solution.

TABLE I

Ca taken mg	*Ca found mg*	*Deviation*
10.00	10.00	0.00
	10.01	+0.01
5.00	5.00	0.00
	5.00	0.00
	5.00	0.00
5.00 + 5 mg Mg	5.00	0.00
	5.01	+0.01
2.50	2.51	+0.01
	2.52	+0.02
	2.52	+0.02
2.50 + 5 mg Mg	2.51	+0.01
	2.52	+0.02
1.00	1.00	0.00
	1.02	+0.02
1.00 + 5 mg Mg	0.99	−0.01

Cyanide should be added before the indicator, otherwise the red colour disappears shortly after it has developed, probably owing to the destruction of the complex in alkaline solution in the absence of excess reagent. The effect of cyanide in the stabilization of the colour is not fully understood.

Under the above conditions barium and strontium interfere.

ACKNOWLEDGEMENT

The author is greatly indebted to Prof. FRITZ FEIGL for his constant interest, to Dr. E. BAYER for donating a sample of the reagent, and to the Conselho Nacional de Pesquisas for financial support.

SUMMARY

Glyoxal bis-(2-hydroxy-anil) is proposed as a new indicator for the complexometric titration of calcium. The end-point is indicated by a sharp change from pink to yellow.

RÉSUMÉ

Un nouvel indicateur, le glyoxal bis-(2-hydroxyanile), est proposé pour le titrage complexométrique du calcium.

ZUSAMMENFASSUNG

Glyoxal bis-(2-hydroxy-anil) wird als neuer Indikator für die komplexometrische Titration von Calcium vorgeschlagen. Der Endpunkt wird durch einen scharfen Umschlag von Rosa nach Gelb angezeigt.

REFERENCES

[1] E. BAYER, *Chem. Ber.*, 90 (1957) 2325.
[2] D. GOLDSTEIN AND C. STARK-MAYER, *Anal. Chim. Acta*, 19 (1958) 437.

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PHOTOMETRIC DETERMINATION OF QUATERNARY AMMONIUM COMPOUNDS WITH HEXANITRODIPHENYLAMINE. II

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In an earlier paper[1] it was shown that quaternary ammonium compounds form complexes with hexanitrodiphenylamine which can be extracted with chloroform or methylene chloride from an aqueous solution of pH 10-11.

The solubility of the complexes in the organic solvents varies with the quaternary ammonium ion involved, but methylene chloride is generally a much better solvent than chloroform. In certain cases, however, the extraction cannot be carried out at the pH 10-11 even with methylene chloride. Primarily, compounds containing several quaternary ammonium groups yield precipitates which are insoluble in reasonable amounts of the organic phase. Experiments have not revealed any solvent which gives better results than methylene chloride under these conditions.

Hexanitrodiphenylamine in water is a moderately strong monobasic acid[1], but in an anhydrous solvent of basic character such as pyridine, hexanitrodiphenylamine can be titrated with tetrabutylammonium hydroxide as a dibasic acid[2]. A study of the conditions in water showed that the univalent anion of hexanitrodiphenylamine also reacts further with base in strongly alkaline aqueous solution. The product formed does not give slightly soluble compounds with quaternary ammonium ions. The reaction with base in a strongly alkaline medium is such that it is possible to determine in this medium the quaternary ammonium compounds which are precipitated at pH 11.

HEXANITRODIPHENYLAMINE IN STRONGLY ALKALINE AQUEOUS SOLUTION

Experimental

Absorption spectrum

The reaction in strongly alkaline aqueous medium involves changes in the absorption spectrum of the substance. In Fig. 1 are given the spectra of $2 \cdot 10^{-5}$ *M* solutions of hexanitrodiphenylamine containing varying concentrations of sodium hydroxide. The determinations were made with a Uvispec spectrophotometer (band width about 5 mμ) between 1 and 5 min after the addition of sodium hydroxide. Longer reaction times gave further changes of the absorption spectra when the sodium hydroxide concentration exceeded 0.2 *N*.

Irreversibility of the reaction

If the strongly alkaline solution of hexanitrodiphenylamine is partly neutralized (about pH 11) and tetraethylammonium bromide (TEABr) is added, a complex can be extracted with chloroform. The absorption spectrum of the complex in the region 340–550 mμ was the same as that obtained with a reagent that had not been treated with strong alkali. Possible irreversible reactions do not appear to yield interfering products.

If an excess of TEABr was added, all the univalent anion of hexanitrodiphenylamine could be extracted, and thus the extent of irreversible reactions could be determined.

Method

1.0 mg ($2.3 \cdot 10^{-6}$ M) of hexanitrodiphenylamine was dissolved in sodium hydroxide of the stated strength to a total volume of 50.0 ml. After the stated time 5.00-ml samples were removed and neutralized with conc. hydrochloric acid. 0.2 ml of 1 N NaOH and 1 mg ($5 \cdot 10^{-6}$ M) of TEABr were added, and after cooling to room temperature the solution was extracted with 3 × 3 ml of chloroform. The chloroform phases were combined, diluted to 10.00 ml and 1 mg of tetrabutylammonium iodide (TBAI) was added. The extinction was determined at 420 mμ. The value obtained was compared with that given by a sample untreated with alkali. The irreversible decomposition was calculated from the decrease in extinction. The results are presented in Table I.

Extraction of the complexes from strongly alkaline aqueous solution

Two methods of extraction were compared. In method 1 hexanitrodiphenylamine was added when the extraction was begun, whereas in method 2 the reagent was added to the alkaline aqueous phase 1 min before the quaternary ammonium compound was added and the extraction started.

Method 1. $8 \cdot 10^{-7}$ equivs. of quaternary ammonium compound were dissolved in 25.0 ml NaOH of the given concentration. 10^{-6} mol of hexanitrodiphenylamine was added dissolved in 25.0 ml of methylene chloride and the mixture was shaken for the stated time. The organic phase was drawn off, centrifuged and 2 mg of TBAI added. The extinction was determined at 420 mμ.

Method 2. 25.0 ml of sodium hydroxide solution of the given concentration were mixed with 10^{-6} mol of hexanitrodiphenylamine dissolved in 25.0 ml of methylene chloride. The mixture was shaken for a few seconds so that the hexanitrodiphenylamine passed into the aqueous phase. After 1 min, $8 \cdot 10^{-7}$ equivs. of quaternary ammonium compound were dissolved in the aqueous phase. The mixture was shaken for the stated time and the determination was completed as in method 1.

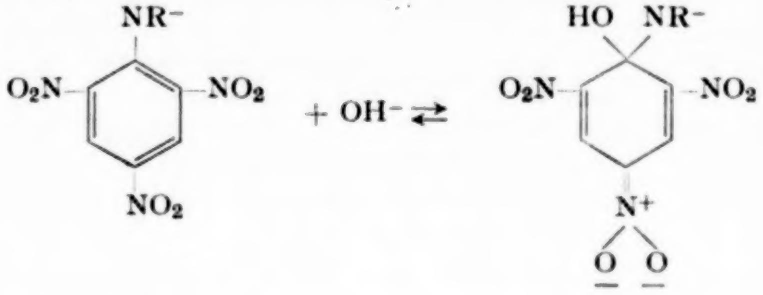
The results are shown in Table II.

DISCUSSION

Hexanitrodiphenylamine is an acid of $pK_a = 2.81$. At pH above 6 it is thus present almost entirely as anion, and its absorption spectrum in aqueous solution remains unchanged up to a pH of about 13. Changes in the absorption spectrum begin to occur when the concentration of alkali in the solvent exceeds 0.1 M and the changes increase markedly with the hydroxide concentration (Fig. 1). From Table I it is evident that less than 10% of the substance is irreversibly changed when the reaction time exceeds 5 min and the concentration of sodium hydroxide $\leqq 2$ N. However the changes in the absorption spectra are too great to depend solely on these irrevers-

References p. 352

ible reactions, and part of the reactions appear to be reversible. The following reaction is a possibility:



or written in a simplified way

$$He^- + OH^- = HeOH^{-2} \quad . . . . \quad (1)$$

The assumption of an equilibrium is also supported by the results obtained by extraction of the complexes with quaternary ammonium ions from a strongly alkaline solution.

In the aqueous solution the following equilibrium may be assumed to exist (besides **1**)

$$He^- + Kv^+ = KvHe(aq) \quad . . . . \quad (2)$$

On shaking with methylene chloride the partition equilibrium appears to be

$$KvHe(aq) = KvHe(org) \quad . . . . \quad (3)$$

(Kv^+ = quaternary ammonium ion).

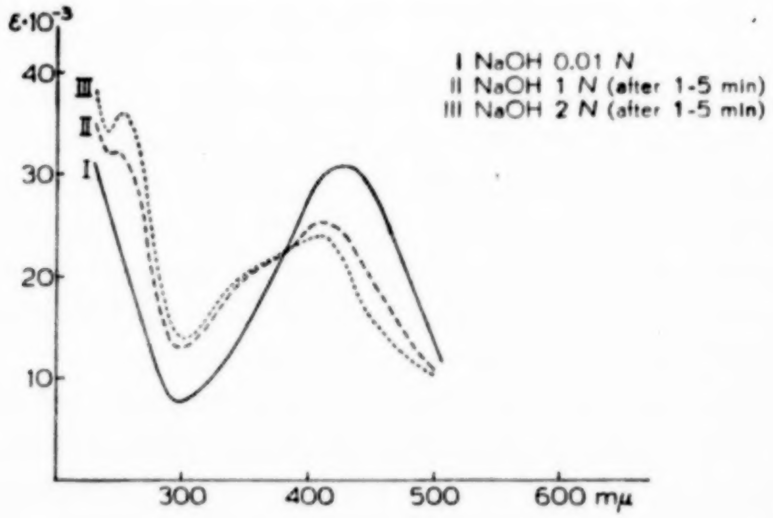


Fig. 1. Absorption spectra of hexanitrodiphenylamine in sodium hydroxide solutions of different concentration.

TABLE I

IRREVERSIBLE CONVERSION (IN %) OF HEXANITRODIPHENYLAMINE IN AQUEOUS SOLUTIONS CONTAINING VARYING CONCENTRATION OF NaOH

Time (min)	*Molar concentration of NaOH*				
	0.01	*1*	*2*	*3*	*4*
5	—	7	9	15	16
10	—	10	15	21	22
30	—	20	31	47	50
60	0	38	53	61	71

TABLE II

TRACTION OF QUATERNARY AMMONIUM COMPLEXES OF HEXANITRODIPHENYLAMINE FROM STRONGLY ALKALINE SOLUTION

Aqueous phase	*Shaking period (sec)*	*Quaternary ammonium ion*					
		Pentamethonium		*Hexamethonium*		*Tetraethylammonium*	
		1	*2*	*1*	*2*	*1*	*2*
	5	0.54	0.26	0.74	0.42	0.74	0.26
	15	0.54	0.41	0.77	0.56	0.82	0.49
NaOH 2 *N*	60	0.53	0.47	0.78	0.71	0.98	0.83
	300	0.45	—	0.83	—	1.02	1.01
	5	0.32	0.03	0.52	0.04	0.63	0.07
	15	0.26	0.05	0.47	0.07	0.65	0.09
NaOH 3 *N*	60	0.16	0.10	0.40	0.08	0.70	0.23
	300	0.11	0.11	0.39	0.32	0.97	0.87

1. Hexanitrodiphenylamine dissolved in methylene chloride was added at the same time as the shaking was started.
2. Hexanitrodiphenylamine was added to the aqueous phase 1 min before the shaking was started.

Organic solvent: CH_2Cl_2. In the table $E^{1\,cm}$ at 420 mμ is given for the organic phase after the shaking.

From Table II it is seen that the amount of complex in the organic phase KvHe (*org*) is markedly altered on a change in the alkalinity of the aqueous phase. Higher concentrations of NaOH give lower final concentrations of KvHe(*org*), possibly because a greater part of the hexanitrodiphenylamine is changed to $HeOH^{-2}$.

It has been reported[2–5] that reactions analogous with 1 attain their equilibria slowly. This can explain why remarkably low values are obtained when hexanitrodiphenylamine is allowed to react in the strongly alkaline solution 1 min before the extraction is started (method 2, Table II). By this method the reagent at the beginning of the extraction occurs chiefly as $HeOH^{-2}$, and the slow reaction (1) gives rise to low initial concentration of He^- and KvHe(*org*). When the extraction is started with hexanitrodiphenylamine chiefly as He^- (method 1) the initially obtained concentration of KvHe(*org*) is markedly higher.

In experiments according to method 1 the concentration of KvHe(*org*) sometimes falls and sometimes rises on prolonged shaking, probably because the partition equilibrium is not reached immediately even on intensive shaking. The concentration of $HeOH^{-2}$ obtained at the beginning can be higher or lower than the final concentration depending on the partition coefficient of the complex. In any case, the slow change of the concentration of KvHe(*org*) by prolonged shaking may be assumed to depend mainly on reaction (1).

PROPERTIES OF THE COMPLEXES

Experimental

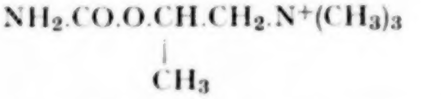
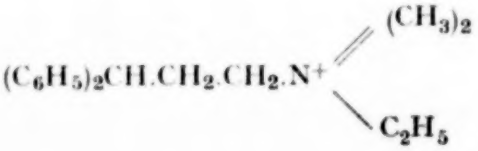
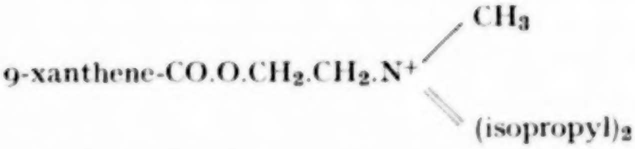
Extraction

For extraction of the complexes the following three methods have been employed: 1. Extraction with chloroform from an aqueous phase at pH 11. 2. Extraction with methylene chloride from an aqueous phase at pH 11. 3. Extraction with methylene chloride from strongly alkaline aqueous phase (3 *N* NaOH).

Details of the methods are given on page 349. No TBAI was added to the solutions of the complexes in the organic solvent. The results with different types of quaternary ammonium compounds are shown in Tables III and IV.

TABLE III

EXTRACTION OF COMPOUNDS CONTAINING ONE QUATERNARY AMMONIUM GROUP AS COMPLEXES WITH HEXANITRODIPHENYLAMINE

Substance	*Formula of the cation*	*Method*		
		1	*2*	*3*
Tetramethylammonium iodide (TMAI)	$(CH_3)_4N^+$	—	—	+
Tetraethylammonium bromide (TEABr)	$(C_2H_5)_4N^+$	+	+	+
Tetrabutylammonium iodide (TBAI)	$(C_4H_9)_4N^+$	—	—	+
Choline chloride	$HO.CH_2CH_2.N^+(CH_3)_3$	o	+	—
Carbamylcholine chloride	$NH_2.CO.O.CH_2.CH_2.N^+(CH_3)_3$	—	+	—
Bethanechol chloride	 $NH_2.CO.O.\underset{CH_3}{\underset{\mid}{CH}}.CH_2.N^+(CH_3)_3$	—	+	—
Neostigmine bromide	$(CH_3)_2N.CO.O.C_6H_4.N^+(CH_3)_3$ (m)	+	+	—
Cetiprine ® bromide	 $(C_6H_5)_2CH.CH_2.CH_2.N^+ \begin{matrix} (CH_3)_2 \\ C_2H_5 \end{matrix}$	—	—	+
Propantheline bromide	 9-xanthene-$CO.O.CH_2.CH_2.N^+ \begin{matrix} CH_3 \\ (\text{isopropyl})_2 \end{matrix}$	—	—	+
Dylamon ® bromide	$(C_6H_5)_2CH.O.CH_2.CH_2.N^+(CH_3)_3$	—	—	+
Methylatropine bromide	—	+	+	+
Methylhomatropine bromide	—	—	+	+
Methylscopolamine nitrate	—	—	+	—

+ = quantitative extraction. — = incomplete extraction. o = no extraction.
Method 1: Extraction with chloroform from an aqueous phase of pH 11. Method 2: Extraction with methylene chloride from an aqueous phase of pH 11. Method 3: Extraction with methylene chloride from a strongly alkaline phase (3 *N* NaOH).

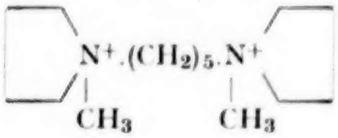
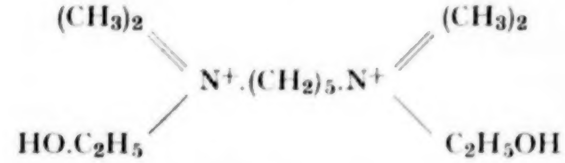
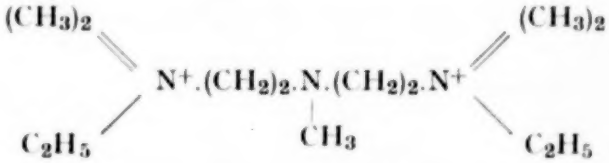
Stability

The majority of the complexes exhibit very good stability in the organic solution, and the extinction is unchanged for several hours. However, some compounds yield less stable complexes with hexanitrodiphenylamine (Table V).

Especially noticeable is the decrease in extinction of the pentamethonium complex, which is largely due to the fact that the complex precipitates. In Fig. 2 are

TABLE IV

EXTRACTION OF COMPOUNDS CONTAINING SEVERAL QUATERNARY AMMONIUM GROUPS AS COMPLEXES WITH HEXANITRODIPHENYLAMINE

Substance	*Formula of the cation*	*Method*		
		1	*2*	*3*
Pentamethonium bromide	$(CH_3)_3N^+.(CH_2)_5.N^+(CH_3)_3$	o	—	+
Pentolinium tartrate		o	—	+
Agentit ® chloride		—	+	—
Hexamethonium bromide	$(CH_3)_3N^+ . (CH_2)_6.N^+(CH_3)_3$	o	—	+
Azamethonium bromide		—	—	+
Gallamine triethiodide	$C_6H_3\,(O.CH_2.CH_2.N^+(C_2H_5)_3)_3$ (1,2,3)	—	—	+
Tubocurarine chloride	—	+	+	o

+ = quantitative extraction. — = incomplete extraction. o = no extraction.
Method 1: Extraction with chloroform from an aqueous phase of pH 11. Method 2: Extraction with methylene chloride from an aqueous phase of pH 11. Method 3: Extraction with methylene chloride from an strongly alkaline aqueous phase (3*N* NaOH).

TABLE V

CHANGES IN MOLAR EXTINCTION OF COMPLEXES ON STORAGE

Quaternary ammonium ion	*Method*	*Molar extinction · 10⁻⁴*	
		After 5 min	*After 18 h*
Pentamethonium	3	5.36	0.56
Azamethonium	3	5.92	5.68
Agentit ®	2	5.80	5.64
Pentolinium	3	6.10	5.78

shown extinction curves for a solution of the pentamethonium complex 5 min (II) and 18 h (III) after its preparation. Curve I was obtained after addition of a large excess of TBAI (5 mg to 50 ml of solution). Solution I is stable and exhibits no change in extinction even after several days.

The varying stability of the complexes is also reflected in the behaviour on filtration. In Table VI are compared the results from determinations when each extracted portion was filtered through paper (Munktell no. 3; 5 cm in diam.) with the values obtained without filtration. The extinction after addition of TBAI (5 mg per 50 ml) is also given in this table.

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TABLE VI

EXTINCTION OF COMPLEXES PREPARED WITH AND WITHOUT FILTRATION OF THE SOLUTIONS IN ORGANIC SOLVENTS

Quaternary ammonium ion	*Method*	*Solvent*	*Molar extinction · 10⁻⁴*					
			350 mμ		*420 mμ*			
			filt.	*unfilt.*	*filt.*	*filt. + TBAI*	*unfilt.*	*unfilt. + TBAI*
Tetraethylammonium	1	$CHCl_3$	1.40	1.37	2.92	3.15	3.15	3.15
Tetraethylammonium	2	CH_2Cl_2	1.32	1.32	3.14	3.15	3.15	3.15
Carbamylcholine	2	CH_2Cl_2	1.32	1.34	2.93	3.15	3.08	3.15
Tubocurarine	1	$CHCl_3$	2.60	2.54	5.80	6.30	5.90	6.30

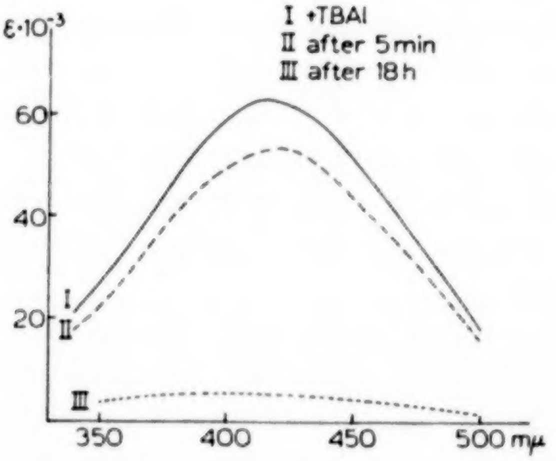

Fig. 2. Absorption spectra of the pentamethonium complex with hexanitrodiphenylamine in methylene chloride after storage and after addition of TBAI.

TABLE VII

EXTINCTION OF COMPLEXES BEFORE AND AFTER ADDITION OF TBAI TO SOLUTIONS OF THE COMPLEXES IN ORGANIC SOLVENTS

Cation	*Number of quatern. ammonium groups*	*Method*	*Molar extinction at 420 mμ × 10⁻⁴*	
			Without TBAI	*With TBAI*
Tetramethylammonium	1	1	3.15	3.15
Tetraethylammonium	1	1,2,3	3.15	3.15
Tetrabutylammonium	1	3	3.15	3.15
Choline	1	2	3.04	3.12
Carbamylcholine	1	2	3.08	3.15
Neostigmine	1	1	2.94	3.15
Methylatropine	1	2	3.04	3.15
Pentamethonium	2	3	5.36	6.30
Agentit ®	2	2	5.60	6.32
Hexamethonium	2	3	6.06	6.32
Decamethonium	2	3	6.08	6.30
Gallamine	3	3	9.09	9.42

Molar extinction

With the help of the methods which, according to Tables III and IV, gave complete extraction, molar extinctions were determined for the complexes of a number of quaternary ammonium compounds of different types. The determinations were carried out at the extinction maximum (420 mμ) before and after addition of TBAI (5 mg per 50 ml). The results are presented in Table VII. The extinction measurements were always made within 5 min after completed extraction. The molecular weights of the quaternary ammonium salts employed were determined by argentimetric titration.

DISCUSSION

Method 3, *i.e.*, extraction with methylene chloride from strongly alkaline medium, seems to be the most general method of extraction according to the experiments in Tables III and IV. The phenol tubocurarine and the easily hydrolysable phenol ester neostigmine cannot be determined according to this principle, since in the strongly alkaline aqueous solution they occur as water-soluble phenolates. The alcohols Agentit ® and choline as well as the choline derivatives (esters) carbamylcholine and bethanechol also cannot be determined by this method. The quaternary tropine esters methylatropine and methylhomatropine are probably rapidly hydrolysed in the alkaline solution, and the extracted complex probably does not contain the acid component of the ester.

Compounds containing several quaternary ammonium ions and which do not have an alcoholic and phenolic character appear to be determinable only by method 3, and some of them cannot be extracted with chloroform (method 1).

Instability in organic media has been found only for the complexes of some cations containing two quaternary ammonium groups (Table V). Among these the pentamethonium complex assumes a distinct position by formation of a precipitate within a few min. If TBAI is added to a more or less changed solution of this complex, the precipitate goes into solution and the solution obtained has the same absorption spectrum as a newly extracted solution of pentamethonium complex mixed with TBAI.

The methylene chloride solution obtained on extraction seems to be supersaturated with regard to the pentamethonium complex. This can be explained by the earlier assumption that the above equilibrium (1) is attained slowly. In method 3 the concentration of He^- at the beginning of the extraction is higher than the equilibrium concentration and the concentrations of KvHe(*aq*) and KvHe(*org*) become too high, (*cf.* Table II, method 1), which results in a supersaturated organic phase.

Table VI shows that filtration causes alterations in the adsorption spectra of the complex solutions; the extinction at 350 mμ remains almost unchanged, whereas that at 420 mμ is noticeably decreased. This change is obtained if part of the complex is converted to free hexanitrodiphenylamine (the extinction curves for complex and free hexanitrodiphenylamine intersect in the region 350–360 mμ[1]). After addition of TBAI the extinction values are the same in both filtered and unfiltered solutions. The filter paper does not absorb the hexanitrodiphenylamine component of the complex, but it seems to have a cation-exchanging effect; Kv^+ is replaced by H^+.

In the foregoing the compounds extracted with organic solvents have been designated complexes without any explanation. The alternative is to consider them as ion pairs, but the molar extinctions of a number of compounds presented in Table VII speak in favour of the former opinion. The cations have no absorption at 420 mμ where the anion has its extinction maximum; if the compounds occurred as ion pairs, all these should have the same extinction per equivalent at this wavelength. In this case the extinction per equiv. varies with the quaternary ammonium ion included; it is probable that another type of compound is formed and this is designated as a complex.

If a large excess of TBAI is added to the organic solution, the same extinction per equiv. of quaternary ammonium compound is obtained, *i.e.* the molar extinction of the TBAI complex.

As stated above TBAI is suitable for stabilizing less stable complex solutions. All the complex solutions investigated have exhibited such good stability as to stand evaporation without alteration in molar extinction.

STANDARD METHODS AND DETERMINATION IN MIXTURES

Experimental

Standard methods

Method 1. $3\text{–}10 \cdot 10^{-7}$ equivalents of quaternary ammonium compound are dissolved in water to a volume of 5.0 ml, mixed with 0.3 ml of 0.1 *N* NaOH, 5 ml of chloroform and 5.0 ml of hexa-chloroform-R. After shaking for at least 15 sec the organic phase is drawn off (without filtration), and the extraction is repeated with chloroform in 5-ml portions until the organic phase remains colorless. The chloroform fractions are combined and diluted with chloroform to an exact volume (usually 50.0 ml), and 5 mg of TBAI are added per 50 ml of the organic solution. The extinction of the solution is determined at 420 mμ.

Method 2. This method is analogous to method 1 but methylene chloride is used instead of chloroform and hexa-methylene chloride-R instead of hexa-chloroform-R.

Method 3. $3\text{–}10 \cdot 10^{-7}$ equivs. of quaternary ammonium compound are dissolved in water to a volume of 5.0 ml, mixed with 20 ml of methylene chloride, 5.0 ml of hexa-methylene chloride-R and 2.0 ml of 10 *N* NaOH. The mixture is shaken for about 10 sec, and thereafter the methylene chloride phase is drawn off (without filtration). To the aqueous phase are added 5 ml of methylene chloride, and the mixture is shaken vigorously for 1 min. 1.0 ml of hexa-methylene chloride-R is added, and the mixture is shaken for 10 sec more. The organic phase is drawn off. Extraction in the manner described is repeated until the organic phase remains colorless. The methylene chloride fractions are combined and diluted with methylene chloride to an exact volume (usually 50.0 ml), and 5 mg of TBAI are added per 50 ml of the organic solution. The extinction of the solution is determined at 420 mμ.

Methylene chloride. The commercial product of boiling point stated as 41° is purified by shaking with a sodium carbonate solution and water. After being dried with calcium chloride it is distilled and the fraction of boiling point 40–41° is collected.

Chloroform. Pharmacopoeial grade.

Hexanitrodiphenylamine. Dipicrylamine p.a. is dissolved in the smallest possible volume of 1 *N* NaOH and the pH of the solution is adjusted to 10 with 1 *M* H_3PO_4. Kieselguhr is added until an almost dry mixture is obtained; this is packed into a chromatographic tube (percolator) and eluted with chloroform until all pentanitrodiphenylamine is extracted, *i.e.* the eluate gives the extinction curve of pure hexanitrodiphenylamine[1]. The contents of the tube are removed and acidified with phosphoric acid (conc. phosphoric acid is added in small portions with intensive mixing until the color of the kieselguhr phase becomes slightly yellow). The kieselguhr phase is packed into the percolator and extracted with chloroform. The eluate is evaporated at diminished pressure to a small volume, and then the precipitated hexanitrodiphenylamine is filtered off and dried protected from basic fumes. A chromatographic control of the purity can be made[1].

Hexa-methylene chloride-R. A 10-mg sample of hexanitrodiphenylamine is dissolved in 100 ml of methylene chloride.

Hexa-chloroform-R. A 10-mg sample of hexanitrodiphenylamine is dissolved in 100 ml of chloroform.

Blank determinations

The determinations were carried out by the methods described under STANDARD METHODS. However, in all determinations 3 ml of hexa-R and 2 ml of organic solvent were added at the first extraction instead of 5 ml of hexa-R. The extraction was continued with 3 portions of the quantity and kind of extraction agent stated in the method and then the solution was diluted to 50.0 ml. After addition of TBAI the extinction was determined in a 1-cm cuvette at 420 mμ. Along with the true blank determinations, tests were also made on samples containing a high concentration of sodium and potassium ions at pH 11. Results are shown in Table VIII.

TABLE VIII

BLANK DETERMINATIONS

Method	*Aqueous phase*	*Organic phase*	$E^{1\,cm}$ *at 420 mμ*		
1	0.006 *N* NaOH	$CHCl_3$	0.005	0.005	0.008
2	0.006 *N* NaOH	CH_2Cl_2	0.008	0.011	0.009
3	3 *N* NaOH	CH_2Cl_2	0.008	0.005	0.007
2	0.006 *N* NaOH + 2 *M* NaCl	CH_2Cl_2	0.06	0.09	
2	0.006 *N* NaOH + 2 *M* KBr	CH_2Cl_2	0.05	0.02	

Determination of quaternary ammonium compounds in the presence of amines

The determinations were carried out by the standard methods above. The results are presented in Table IX.

TABLE IX

DETERMINATION OF QUATERNARY AMMONIUM COMPOUNDS IN THE PRESENCE OF AMINES

Sample	*Method*	*Amount mg*	
		calc.	*found*
1. Methylatropine bromide	2	0.300	0.303
Atropine sulfate		0.200	—
2. Methylscopolamine bromide	2	0.302	0.305
Scopolamine bromide		0.204	—
3. Cetiprine ® bromide	3	0.302	0.306
Mepyramine maleate		0.202	—

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Determination of quaternary ammonium compounds in mixtures

Determinations were only carried out with mixtures where only one component was extractable with chloroform at pH 11.

Method: In a sample containing at the most 10^{-6} equivs. of quaternary ammonium compounds the component extractable with chloroform was determined using *standard method* 1, but with filtration of the chloroform phases through a paper filter which was afterwards washed with chloroform.

The component extractable with methylene chloride was then determined. The aqueous phase weakly acidified and shaken in order to dissolve any precipitated complex. The determination was continued according to *standard method* 3, but each methylene chloride phase was passed through the previously mentioned filter. When the extraction was completed, the filter was washed with 5 mg of TBAI dissolved in 5 ml of methylene chloride in order to dissolve any precipitate, and then with at least 5 ml of methylene chloride. No more TBAI was added before the final photometric measurement.

The results are presented in Table X.

TABLE X

DETERMINATION OF QUATERNARY AMMONIUM COMPOUNDS IN MIXTURE

Sample	*Amount* mg	
	calc.	*found*
1. Tetraethylammonium bromide	0.170	0.169
Pentolinium tartrate	0.205	0.203
2. Methylatropine bromide	0.150	0.147
Hexamethonium bromide	0.101	0.104
3. Neostigmine bromide	0.153	0.153
Pentolinium tartrate	0.122	0.123

DISCUSSION

The standard methods proved to be applicable for all quaternary ammonium compounds tested (medically used parasympatholytic, neuromuscular blocking and ganglionic blocking substances). A total volume of 50 ml was sufficient for all compounds except pentamethonium, where a total volume of 100 ml was used. The sample amounts employed, $(3\text{–}10 \cdot 10^{-7})$ equivs., give an extinction of 0.2 – 0.6 in a total volume of 50.0 ml and a 1-cm cuvette. It is possible to use smaller samples, but then after addition of TBAI the solution of the complex should be evaporated to a smaller volume before the final determination of the extinction.

From Table VIII it is seen that the blanks in all three methods are insignificant. The amount of reagent employed in the blank determinations corresponds to the excess of hexanitrodiphenylamine which is obtained when the sample contains $4 \cdot 10^{-7}$ equivs. of quaternary ammonium compound. A high content of sodium ions yields large blank values at pH 11, but in strongly alkaline solution the high sodium ion content is without greater significance. Presumably the sodium salt of hexanitrodiphenylamine is somewhat soluble in the organic phase, but in the more

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alkaline solution the reagent does not occur as univalent anion and thus is not extractable as sodium salt. The interfering effect of potassium is probably caused primarily by the precipitation of hexanitrodiphenylamine by this ion.

Amines do not seem to interfere in the determination of quaternary ammonium ions. Some amines form complexes with hexanitrodiphenylamine which are extractable with chloroform or methylene chloride, but in the standard methods such a high pH is used that most amines occur almost entirely as the free base, which does not yield extractable compounds with hexanitrodiphenylamine.

The method given for determination of quaternary ammonium ions in mixture has, previously mentioned, a limited application. Procedures based on chromatographic partition methods should, however, afford increased possibilities of separation.

SUMMARY

In strongly alkaline medium (more than 0.1 N NaOH) hexanitrodiphenylamine anion reacts with base. The reaction is rather slow and is partly reversible.

Quaternary ammonium ions can be determined by extraction of their hexanitrodiphenylamine complexes with chloroform or methylene chloride at pH 11 or with methylene chloride from 3 N NaOH. Only the latter method is applicable to compounds containing several quaternary ammonium groups. The compounds extracted have high molar extinction and good stability. Quaternary ammonium ions can be determined in the presence of amines, and in some cases determination of quaternary ammonium ions in admixture is possible.

RÉSUMÉ

Une méthode est proposée pour le dosage photométrique des ions ammonium quaternaire au moyen d'hexanitrodiphénylamine. Les complexes formés sont extraits par le chloroforme ou par le chlorure de méthylène. Ils présentent alors une extinction moléculaire élevée et une bonne stabilité.

ZUSAMMENFASSUNG

Quaternäre Ammonium-Ionen können mit Hilfe von Hexanitrodiphenylamin photometrisch bestimmt werden. Die gebildeten Komplexe lassen sich aus einer wässrigen Lösung mit Chloroform oder Methylenchlorid extrahieren. Sie sind sehr stabil und besitzen eine hohe molare Extinktion.

REFERENCES

[1] G. Schill and B. Danielsson, *Anal. Chim. Acta*, 21 (1959) 248.

[2] J. S. Fritz, A. J. Moye and M. Johnson Richard, *Anal. Chem.*, 29 (1957) 1685.

[3] G. Briegleb and G. Angerer, *Angew. Chem.*, 64 (1952) 685.

[4] H. Brockman and E. Mayer, *Naturwissenschaften*, 40 (1953) 242.

[5] G. Briegleb and G. Angerer, *Naturwissenschaften*, 40 (1953) 107.

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DETERMINATION OF MICROGRAM QUANTITIES OF URANIUM IN THORIUM

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In the analysis of thorium of nuclear purity, a method was required for the determination of uranium in thorium at a level of about 1 p.p.m. Several methods have been reported for the separation and determination of uranium in thorium. WILLIAMS[1] used an alumina-cellulose chromatographic column and extracted uranium with ether containing 1% nitric acid. The uranium was then determined either spectrophotometrically or fluorimetrically. The method is satisfactory above 50 p.p.m. of uranium; at lower concentrations all reagents (particularly alumina) have to be first washed thoroughly with ether. EBERLE AND LERNER[2] separated uranium from thorium by extraction with tributyl phosphate (TBP); for a good separation, the organic phase containing the extracted uranium must be washed many times, first with hydrochloric acid and then with nitric acid. CLINCH AND GUY[3] extracted uranium as the thiocyanate complex into TBP, using EDTA to prevent the extraction of iron and some other elements. However, they recommend a preliminary separation of the uranium by ether extraction before applying the method to thoria samples; at low levels of uranium, the accuracy is not satisfactory. HARDWICK AND MORETON-SMITH[4] have recently reported a method for the separation of ^{233}U from irradiated thorium by extraction of the diethyl dithiocarbamate complex of uranium with hexone. The method was improved[5] by extraction of the oxine complex of uranium with chloroform in the presence of EDTA. In either method the ^{233}U is determined by α-counting.

The most sensitive method for the determination of microgram quantities of natural uranium is by measurement of its fluorescence in fused sodium fluoride melts[6]. Uranium must be in a fairly pure form because most other elements, including thorium, have a quenching effect on the fluorescence. This paper presents a method of separating uranium from thorium by means of TBP in the presence of EDTA as complexing agent. Although CLAYTON *et al.*[5] have reported that this extraction of uranium is not satisfactory, their conditions of pH, etc. were not described. The recovery of uranium by the proposed method was found to be quantitative within the limits of accuracy of the fluorimetric method of determination. The method was satisfactory for thoria samples having an uranium content of as low as 0.4 p.p.m. and it may be possible to extend it to other ranges by suitable adjustment of sample size.

EXPERIMENTAL

Apparatus

1. Fluorimeter, A.E.R.E., Harwell, Model 1080A; 2. pH meter; 3. separatory funnels, Squibb pear-shaped, 125-ml and 250-ml capacity.

Reagents

1. EDTA, disodium salt, A.R. Grade; 2. calcium nitrate, crystalline, A.R. Grade; 3. nitric acid, A.R. Grade; 4. ammonium hydroxide, liquor ammonia, A.R. Grade, diluted 1:1; 5. ammonium nitrate solution. Saturated aqueous solution of ammonium nitrate (A.R. Grade) adjusted to pH 2.5 with dilute nitric acid; 6. ammonium carbonate solution. 5% (W/V) Aqueous solution of ammonium carbonate, A.R. Grade; 7. tributyl phosphate, 5% solution. The commercial TBP was washed with a 5% solution of sodium carbonate to remove any mono- or di-butyl phosphate present, and then several times with distilled water to remove the carbonate. It was then diluted with kerosene or white spirit to give a 5% (V/V) solution. This solution was equilibrated with an equal volume of dilute nitric acid of pH 2.5, and was, after separation, ready for use.

Principle of the method

To the thorium in the form of a nitrate solution, EDTA is added in slight excess over the equimolecular ratio and the pH is adjusted. Salting agent is added and the uranium extracted with 5% TBP solution. The organic layer is scrubbed with saturated ammonium nitrate solution and the uranium back-extracted into 5% ammonium carbonate solution. Uranium is then determined fluorimetrically.

Salting agent

Various salting agents have been recommended[7] to assist the extraction of uranyl nitrate by TBP. Sodium, calcium and aluminium nitrates were studied for their salting effect in the present method. The extraction in the presence of sodium nitrate was not quite satisfactory, whereas aluminium nitrate caused the extraction of thorium into TBP, even when EDTA was present. Calcium nitrate was found to be satisfactory. It is considered that calcium nitrate not only acts as a salting agent, but also associates with the excess EDTA and thus helps in the extraction of uranium. For quantitative recovery it was necessary almost to saturate the aqueous phase with calcium nitrate and to carry out 5 successive extractions with TBP using a volume almost equal to that of the aqueous phase each time.

Effect of pH

CABELL[8] has reported that uranium forms complexes with EDTA at a pH of about 3 to 5, although these may be weak. It was, therefore, expected that the pH of the aqueous phase would have a considerable effect on the extraction of uranium. The effect of pH was studied over the range 1–4, and it was found that the recovery of uranium was quantitative between pH 2 and 3.5. Below pH 2 considerable quantities of thorium ($>$ 0.5 mg) were extracted owing to the instability of the thorium–EDTA complex. For all further work the pH was adjusted to approximately 2.5 by means of indicator paper. At this pH the amount of thorium extracted was only about 2 μg, which did not interfere in the final fluorimetric determination.

Interferences

The interferences of several common cations and anions were investigated. The ions were added as shown in Table I; no interference was observed. Much greater amounts of these impurities could probably be tolerated.

TABLE I

INTERFERENCES STUDIED

Ion	*Quantity added* μg	*Ion*	*Quantity added* μg
Fe^{+3}	400	Cr^{+3}	40
Al^{+3}	200	Ni^{+2}	100
Ce^{+4}	100	Co^{+2}	40
Ti^{+4}	40	Mg^{+2}	200
Cu^{+2}	200	SO_4^{-2}	500
Zn^{+2}	100	PO_4^{-3}	500
Cd^{+2}	40	F^-	500
Pb^{+2}	200	MoO_4^{-2}	100
Sn^{+2}	100	VO_3^-	40
Bi^{+3}	40		

PROCEDURE

An aliquot of the sample was taken containing about 1 g of ThO_2 as the nitrate. If the sample contained organic matter it was evaporated in a platinum dish and ignited in a furnace at 600° to destroy all organic matter. The residue was dissolved in nitric acid with a few drops of dilute hydrofluoric acid (2%) and the solution was evaporated to dryness. The residue was then taken up with a few ml of nitric acid and again evaporated to dryness.

The dried residue was dissolved in 5 ml of water, 1.6 of EDTA was added and the pH of the solution adjusted to 2.5 with the help of indicator paper. Dry crystalline calcium nitrate (16 g) was added and the volume adjusted to 25 ml with water. The solution was then transferred to a 125-ml separatory funnel and 20 ml of equilibrated 5% TBP were added after rinsing the beaker with the same TBP. The funnel was shaken vigorously for one min, and the two layers allowed to separate. The aqueous layer was drawn off into the original beaker and the organic layer transferred to a 250-ml separatory funnel using a few ml of TBP solution to rinse the funnel stem. The extraction procedure was repeated four times and the TBP layers combined in the second separatory funnel. The combined organic phase was then scrubbed with saturated ammonium nitrate (adjusted to pH 2.5) three times to remove the small quantities of aqueous phase mechanically carried over. The uranium was stripped from the TBP extract with one 10-ml portion of distilled water, one 10-ml portion of 5% (W/V) solution of ammonium carbonate and finally with two 10-ml portions of water containing 1 ml of ammonium carbonate solution. All the uranium strippings were collected in a porcelain dish, acidified with nitric acid, and evaporated to dryness slowly over a burner. The dried residue was then ignited at 600° in a muffle furnace. The residue was taken up with dilute nitric acid, transferred to a 5-ml volumetric flask and the volume made up. Uranium was then determined fluorimetrically.

Results on synthetic samples are shown in Table II. Various quantities of uranium in the range 1 to 10 μg were added to aliquots of thorium nitrate solution containing approximately 1 g ThO_2, and the uranium content determined. A blank was run on all the reagents used, and amounted to 0.32 μg uranium. In experiment 7, 2.5 g of

ThO_2 were taken, thus extending the limit of determination to 0.4 p.p.m. of uranium in ThO_2.

TABLE II

ANALYSIS OF SYNTHETIC SAMPLES

Sr.No.	*Uranium added* µg	*Uranium found* µg	*Difference* µg
1	1.00	1.08	+ 0.08
2	2.00	1.88	— 0.12
3	3.00	2.98	— 0.02
4	5.00	5.05	+ 0.05
5	7.00	7.08	+ 0.08
6	10.00	10.13	+ 0.13
7	1.00	1.09	+ 0.09

SUMMARY

Uranium present in micro amounts in thorium is extracted with 5% tributyl phosphate in presence of EDTA at pH 2.5. Calcium nitrate is used as salting agent. Uranium is back-extracted with ammonium carbonate and determined fluorimetrically. Thoria samples containing as little as 0.4 p.p.m. of uranium have been analysed.

RÉSUMÉ

Une méthode est décrite pour le dosage de l'uranium, en faibles teneurs, dans le thorium. On procède par extraction; l'uranium est finalement dosé par fluorimétrie.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von kleinen Mengen Uran in Thorium nach dem Extraktionsverfahren mit anschliessender fluorimetrischer Bestimmung des Urans.

REFERENCES

[1] A. F. Williams, *Analyst*, 77 (1952) 297.

[2] A. R. Eberle and M. W. Lerner, *Anal. Chem.*, 29 (1957) 1134.

[3] J. Clinch and M. J. Guy, *Analyst*, 82 (1957) 800.

[4] W. H. Hardwick and M. Moreton-Smith, *Analyst*, 83 (1958) 9.

[5] R. F. Clayton, W. H. Hardwick, M. Moreton-Smith and R. Todd, *Analyst*, 83 (1958) 13.

[6] G. R. Price, R. J. Ferreti and S. Schwartz, *Anal. Chem.*, 25 (1953) 322.

[7] T. W. Bartlett, *U.S. AEC Report* No. K-706, 1951.

[8] M. J. Cabell, *Analyst*, 77 (1952) 859.

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DETERMINATION OF THALLIUM IN BIOLOGICAL MATERIAL

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The use of thallium preparations particularly in rodenticides, as well as industrial exposures to thallium, have caused many cases of poisoning[1] so that it has been necessary to work out reliable methods for the determination of thallium in biological materials. A number of methods has been introduced; these have been reviewed in detail by ANDERSON[2]. Very small amounts of thallium can be determined specifically by spectrography, while the colorimetric methods are usually indirect and often not sufficiently specific. Recently, several new colorimetric methods based on rhodamine B and other reagents have been developed[3].

Dithizone has proved to be an exceedingly useful reagent for the determination of microgram amounts of many heavy metals[4]. The low affinity of dithizone for thallium may introduce difficulties in the development of a method for thallium based on this complexing agent. Dithizone has frequently been suggested for the isolation of thallium but as a rule other methods have been employed in the final estimation. However, BAMBACH[5], using a colorimetric dithizone method, determined lead under such conditions that thallium followed lead, and KAMERMAN[6], after removing interfering metals, determined thallium by titration with a dithizone solution.

In the present investigation conditions have been worked out which produce a stable thallium dithizonate that is well suited for spectrophotometric measurements. After the virtual completion of this work, CLARKE AND CUTTITTA[7] published a method similar to that described herein which was used for the determination of thallium in pure thallium salt solutions.

The existence of a dithizonate of tervalent thallium is uncertain, but monovalent thallium is extracted by dithizone in carbon tetrachloride at an optimal pH of 11[8]. Extraction by dithizone in chloroform is more efficient and at pH 11 or more, approximately 80% of thallium(I) is extracted[4]. At pH values around 11, dithizone reacts with many other metals, which either have to be removed or prevented from reacting with dithizone. Citrate and cyanide are commonly used as masking agents, but not all interfering metals are masked. Cyanide is used here, but fails to mask lead, bismuth and tin, and some other metals, *e.g.* mercury, are masked incompletely. A separation step must therefore precede the final extraction.

The separation is carried out by extraction of thallic chloride with ether and reextraction of thallous chloride into water; the latter procedure was introduced by REITH AND GERRITSMA[9]. Suitable conditions — extraction of thallic chloride with ether from about 1 *N* hydrochloric acid — were selected using the data of IRVING

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* Part of this work was carried out at the State Veterinary Medical Institute, Stockholm 50.

AND ROSSOTTI[10]. Their data also suggested, that hydrochloric acid very probably could be replaced by a sulphuric acid solution containing 1 *M* sodium chloride. Reextraction of thallous chloride into water is easily accomplished.

In the final extraction step dithizone is added in ammoniacal solution in order to reduce interference from chloroform-soluble impurities present in dithizone. Thallium dithizonate and some excess free dithizone are extracted into chloroform. Most of the free dithizone is removed by two washings with a dilute ammoniacal solution; the amount remaining in the chloroform phase does not affect the determination of thallium. The content of thallium is calculated from the absorbance at 510 mμ. Absorption curves for dithizone and thallium dithizonate are shown in Fig. 1.

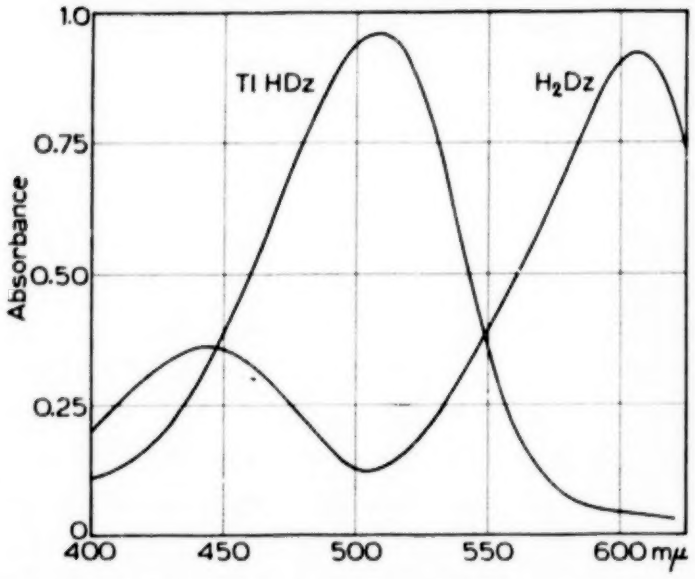

Fig. 1. Absorption curves for dithizone (H_2Dz) and thallium dithizonate (TlHDz) in chloroform. The heights of the maxima at 510 and 605 mμ are not comparable.

The determination of thallium, as outlined above (procedure A), is sufficiently specific for most purposes and is recommended as a standard method. However a few metals, especially when present in relatively large amounts, can interfere. A variation has therefore been worked out (procedure B) where thallium is separated from these metals by decomposing the thallium dithizonate at pH 4.6. The thus purified thallium solution is again extracted with dithizone. Procedure B is a little longer but it is highly specific and more sensitive to very small amounts of thallium in biological material.

APPARATUS AND REAGENTS

Analytical reagents and glass-distilled water are used throughout, except where otherwise stated. Daylight should be excluded during all work with solutions containing chlorine, hypochlorite, dithizone and thallium dithizonate. Consistent cleanliness is most important in this type of work.

Digestion apparatus, according to KLEIN[11], as described in a previous communication[12]. *Separating funnels*, Gilson model, 500, 250 and 125 ml. Only glass stoppers are used for flasks and separating funnels. *Cleaning of glassware.* After use the digestion apparatus is boiled with nitric acid, and before the next analysis boiled with water. Separating funnels, including ground surfaces, and other glassware are cleaned with raw, preferably chlorine-containing, hydrochloric acid and then rinsed very carefully with warm water and distilled water.

Thallium standard, 1 mg Tl/ml. Thallous nitrate (651.7 mg) is dissolved in water and made up to 500 ml.

Diluted thallium standard, 100 μg Tl/ml. Thallium standard is diluted with water (10:100). Stable for one week. *Hypochlorite solution*. Commercial sodium hypochlorite solution containing about 12% active chlorine and kept in the cold. *Chlorine solution*. Water (100 ml), hypochlorite solution (3 ml) and hydrochloric acid (3 *N*, 10 ml) are mixed immediately before use. *Sulphurous acid*. Commercial sulphur dioxide solution containing 5–6% SO_2 and kept cold. *Bromocresol green*, 0.5% in alcohol. *Ammonium hydroxide*, conc., $d = 0.91$. *Acid sulphite solution*. Water (400 ml) is carefully poured on to anhydrous sodium sulphite (25 g). After cooling in the refrigerator sulphuric acid (5 *N*, 50 ml) is added and gently mixed. The solution is kept cold. *Dithizone solution*, 0.5% in chloroform. Keep under a layer of acid sulphite solution in the refrigerator.

Hydroxylamine sulphate, 1 *M*, Hydroxylamine sulphate (16.4 g) is dissolved in water and made up to 100 ml.

Cyanide solution. Potassium cyanide (10 g) is dissolved in water (100 ml). Stable for a few weeks.

Dithizone mixture, prepared immediately before use. x is chosen to give enough mixture for an extraction blank and the samples; in procedure B enough for the second extraction with dithizone also must be taken. With $x = 1$, 37 ml of the mixture are obtained.

In a separating funnel, water ($x \cdot 10$ ml), dithizone solution ($x \cdot 2$ ml) and ammonium hydroxide ($x \cdot 5$ ml) are mixed. The funnel is shaken for 15 sec. After a few min the chloroform phase is discarded and chloroform ($x \cdot 5$ ml) added. After shaking for 5 sec, the chloroform phase is allowed to settle for 5–10 min. The chloroform layer, which should be green, is then discarded. To the separating funnel are now added hydroxylamine sulphate ($x \cdot 2$ ml), ammonium hydroxide ($x \cdot 15$ ml) and cyanide solution ($x \cdot 5$ ml). The contents are mixed.

Wash solution. Ammonium hydroxide (50 ml) and cyanide solution (10 ml) are diluted with water and made up to 1 l. Stable for one or two weeks.

Acetic acid (1:5). Glacial acetic acid (20 ml) is diluted with water to 100 ml (only for procedure B).

Acetate buffer. Sodium acetate trihydrate (27.2 g) and glacial acetic acid (12.0 g) are dissolved in water and diluted to 100 ml (pH about 4.6; only for procedure B).

PROCEDURE A

Combustion. The combustion of the organic material is carried out according to KLEIN[11] as described for the determination of mercury[12]. About 25 g of organs or 10 g of cereals are weighed. Water, nitric acid and boiling stones (quartz, acid washed) are added. To urine (100–500 ml) nitric acid is added and the solution is evaporated in the digestion apparatus to about 50 ml. The size of the sample is dependent upon its content of dry organic material. Samples with a high mineral content, such as bone, give serious bumping; in such cases the amounts weighed should be reduced. During the combustion, nitric and sulphuric acids are added and two distillations into the reflux collector are carried out as previously described[12], heating with a small flame being omitted.

After the second distillation the contents of the reflux collector are not returned to the digestion flask but discarded. The reflux condenser and collector are then removed. Ammonium sulphate (0.5 g) is added[13] through a wide glass tube into the digestion flask. The heating is resumed, gently at first, the central neck being left open. Each time the contents begin to darken, the flame is removed and 0.5–1 ml of nitric acid is added dropwise, splashing being avoided. The heating is gradually increased. When sulphuric acid begins to reflux on the sides of the flask and the contents do not darken any more, the dropping funnel is removed and a glass stopper inserted in its place. The flame is regulated so that sulphuric acid refluxes half-way up the flask walls, and heating is continued for five more min. After combustion the liquid should be nearly colourless. The flask is cooled and stoppered. Work may be interrupted at this point.

Separation. Two 500-ml separating funnels (I and II) are used for each sample. The solution in the digestion flask is diluted with water (50 ml) and filtered into I.

Flask and filter are washed with 50 ml of water (altogether 100 ml of water are added) and sodium chloride (6.5 g) is added and dissolved. Hypochlorite solution (3 ml) is added in portions with swirling, followed after mixing, by ether (125 ml). A 10-ml cylinder is put beneath each separating funnel to catch any drops escaping. The pressure should always be released before shaking when ether is present. The funnel is then shaken vigorously for two min. A moistened potassium iodide-starch paper shows when the vapour phase contains an excess of chlorine. After a minute the water phase is run into II. Chlorine solution (20 ml) is added to the ether in I, which is shaken for 15 sec. The water phase is combined with the first water phase in II. I, containing an ether solution with most of the thallium, is stoppered. (Its stem and the cylinder beneath it are rinsed).

Hypochlorite solution (2 ml) and ether (65 ml) are added to II, which is shaken vigorously for 1 min. The water phase is discarded. Chlorine solution (20 ml) is added and II is shaken for 15 sec. The water phase is again discarded and the ether phase combined with the first ether solution in I. II is rinsed with a small amount of ether. The collected ether extracts are shaken vigorously for 1 min with sulphurous acid (15 ml). A moistened potassium iodide-starch paper, made blue above the chlorine solution, is held in the vapour phase of I. Sulphur dioxide gas should be present in excess and bleach the paper at once. The water phase, containing most of the thallium, is run into a porcelain dish (about 7 × 3 cm). Sulphurous acid (10 ml) is added to I, which is shaken vigorously for 30 sec. The water phase is combined with the solution in the porcelain dish. I is finally shaken for 15 sec with water (5 ml) and the water phase run into the dish. The water solution is evaporated on the steam bath to about one ml. (The determination may be interrupted at this point.)

Water (5 ml) and bromocresol green (1 drop) are added, followed by the dropwise addition of ammonium hydroxide with stirring until the colour changes; usually about 0.7 ml is consumed. Sulphuric acid (1 *N*) is added, also dropwise, until the indicator shows a neutral or acid reaction. In alkaline solution thallous ions are oxidized to thallic hydroxide. The sample is now ready for extraction.

Extraction. A special blank is prepared at the beginning of the extraction. For this extraction blank and for each sample a 250-ml separating funnel (I) and a 125-ml separating funnel (II) are required. Chloroform (50.0 ml) is added to I. For the blank, water (20 ml) is added and for the sample the contents of the porcelain dish. The dish is rinsed with three portions of water (altogether about 13 ml) and the inside walls are rubbed with a glass rod. The volume of the water solution in I is now about 20 ml. Dithizone mixture (40 ml) is added to I, which is shaken vigorously for 1 min.

The chloroform layers are run into II. The water layers are discarded (care: cyanide), and I is rinsed with distilled water. To each of the chloroform solutions is added wash solution (25 ml), and II is shaken for 15 sec. The chloroform layers are run back into I. (When using procedure B, stop at this point and continue under the heading "Procedure B".) The chloroform solutions are shaken a second time for 15 sec with wash solution (25 ml).

A couple of ml of the chloroform layers are withdrawn in order to remove water from the stopcocks. A wad of cotton is rinsed with a dilute solution of dithizone in chloroform and with chloroform and pieces are inserted into the stems of I and pushed up against the stopcocks to serve as filters. A couple of ml of the chloroform layers are drawn off through the filters and discarded. The chloroform extract from the sample is read *versus* the extraction blank in 1-cm cells in the spectrophotometer. The absorbance at 510 mμ, A_{510}, is noted.

Calculation. Amount of thallium in the whole sample (or in an aliquot, see below), in $\mu g = k_A \cdot A_{510}$, where k_A is obtained from a standard curve.

Standard curve. The standard curve is prepared by extraction of standard thallium solutions without previous combustion and separation. Four 250-ml separating funnels (I) and four 125-ml separating funnels (II) are required. To I is added chloroform (50.0 ml), water (20, 19, 18 and 17 ml respectively), diluted thallium standard (0, 1.00, 2.00 and 3.00 ml respectively) and dithizone mixture (40 ml). All are shaken vigorously for 1 min. The procedure is continued as described under extraction. The three thallium-containing extracts are read *versus* the extraction blank at 510 mμ.

TABLE I

DETERMINATIONS WITH PROCEDURE A

25 g of human liver were used for each analysis

Liver	*Added*			*Thallium, μg*			*Recovery %*
	Tl μg	*ion*	*mg*	*Found*	*Blank*	*Difference*	
B	50	—	—	57	10	47	94
A	100	—	—	113	11	102	102
B	100	—	—	114	10	104	104
A	200	—	—	218	11	207	103.5
B	250	—	—	275	10	265	106
B	300	—	—	319	10	309	103
C	200	Fe^{II}	100	221	20	201	100.5
D	200	Co^{II} Ni^{II}	50 50	215	10	205	102.5
E	200	Mn^{VII} Pd^{II}	100 50	226	18	208	104
D	200	Pt^{IV}	50	223	10	213	106.5
C	200	Cu^{II}	100	227	20	207	103.5
D	200	Ag^{I} [a]	100	203	10	193	96.5
D	200	Au^{III}	48	213	10	203	101.5
C	200	Zn^{II}	100	221	20	201	100.5
C	200	Cd^{II}	100	630	20	610	305
D	200	Cd^{II}	5	213	10	203	101.5
B	200	Hg^{II}	100	815	10	805	403
C	200	Hg^{II}	10	348	20	328	164
C	200	Hg^{II}	1	237	20	217	108.5
E	200	In^{III}	100	346	18	328	164
D	200	In^{III}	10	236	10	226	113
D	200	Sn^{II}	100	215	10	205	102.5
B	200	Pb^{II}	100	239	10	229	114.5
D	200	Bi^{III}	100	417	10	407	204
D	200	Bi^{III} Cl^-	10 1000	234	10	224	112
D	200	Br^- I^-	500 500	210	10	200	100
D	200	$S_2O_3^{-2}$ SCN^-	500 500	212	10	202	101

[a] Precipitated AgCl was not filtered off.

The values of A_{510} are plotted against the amount of thallium in μg, a straight line standard curve being obtained (Fig. 2). The amount of thallium, corresponding to $A_{510} = 1.000$, is denoted by k_A. A mean value of $k_A = 328$ was obtained.

The blanks. The purpose of the extraction blank is to make the overall blank as low and uniform as possible. Blank determinations on the whole procedures have to be run frequently, and the blank values should be subtracted from the thallium values found. The blank determinations are run on tissue samples which are free of thallium. If tissue samples are not available, other organic matter such as sucrose or filter paper may be employed. The blank values may be due to interfering metals in the sample, chemicals or glass vessels; or it may be caused by an uneven distribution of free dithizone in the chloroform phases or in oxidation products from the dithizone. Blank values for human liver obtained by this procedure are given in Table I.

General remarks

The chloroform layers from blanks are faintly green and those from thallium-positive samples red. When red extracts are obtained, absorption curves should be prepared (*cf.* Fig. 1) and their maxima noted. It is sometimes possible to decide from the position of the maximum on the nature of the metal present. Mercury dithizonate, for instance, has a peak at 490 mμ, which is quite distinct from that of thallium dithizonate, where it is just below 510 mμ.

When it is believed that the sample may contain more than 300 μg of thallium, the contents of the porcelain dish are, after neutralization, quantitatively transferred to a 25-ml volumetric flask and made up to the volume with water. An adequate amount of this solution is added to the separating funnel. Water is also added to bring the volume of the aqueous phase to 20 ml.

When 10 g or less of wet tissue is weighed, the amounts of acids, water and other chemicals used during combustion and separation may be reduced by half; 250-ml separating funnels are convenient for the separation, but no changes are necessary for the extraction.

PROCEDURE B

Procedure A is followed to the point indicated above just after the first washing of the chloroform extracts. The procedure is then as follows:

The aqueous phases are discarded and II is rinsed with distilled water. To each of the chloroform solutions are added water (20 ml), bromocresol green (1 drop) and acetic acid (1:5; about 1.6 ml). I is inverted a few times and the colours of the water phases observed. The amount of acetic acid is chosen so as to give a neutral indicator reaction, pH about 4.6. The neutral green colour should persist after shaking. I is then shaken vigorously for 30 sec. The chloroform layers are run into II. Chloroform (25 ml) is added to I, and water (15 ml) and acetate buffer (1 ml) to II, which is then shaken for 30 sec. The chloroform layers are discarded and the aqueous phases are run into I. II is rinsed with water (about 2.5 ml) which is also run into I. The volumes of the water phases in I will now be about 40 ml. II is rinsed with distilled water.

I is shaken for 15 sec, and the chloroform layers are discarded. The water solutions are washed once again by shaking for 15 sec with chloroform (25 ml), and the chloroform layers are discarded. To each of the water solutions are added chloroform (50.0 ml) and dithizone mixture (50 ml). They are then shaken vigorously for 1 min.

The determination is concluded by two washings of the chloroform extracts with wash solution as described under procedure A. The absorption of the solution is then read *versus* the extraction blank.

Calculation

Amount of thallium in the whole sample or in an aliquot, in $\mu g = k_B \cdot A_{510}$, where k_B is obtained from a standard curve. The standard curve is prepared as in procedure A, the extracts being purified as described above. The curve is drawn (Fig. 2), and k_B is read off in the same manner as k_A. A mean value of $k_B = 334$ was obtained.

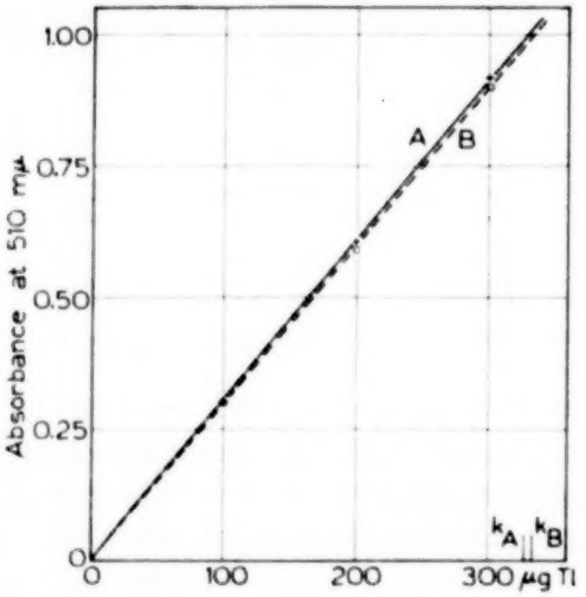

Fig. 2. Standard curves for procedures A and B.

RESULTS AND INTERFERENCES

Procedure A. Table I presents the results of determinations of thallium in liver samples to which diluted thallium standard has been added. The thallium recovered after subtraction of the blank values is given in per cent of thallium added. The method gives slightly high recoveries of about 103%. Thallium seems to be extracted more completely from sample solutions than from standard solutions.

The effects of various cations and anions on the yield of thallium are also shown in Table I. The effects of all known "dithizone metals", except polonium, in amounts up to 50 or 100 mg have been tested. In most cases the added metals interfered little or not at all, but four metals were found to interfere seriously with the thallium analysis; these are mercury in amounts exceeding about 1 mg, and cadmium, bismuth and indium when more than approximately 10 mg were present. In practice with biological samples, cadmium, bismuth or indium contents exceeding 10 mg seldom occur. Mercury contents exceeding 1 mg in 25 g of kidney occur in cases of lethal mercury poisoning. Halogen, thiosulphate and thiocyanate ions had little effect on the determination.

Procedure B. The results of determinations according to procedure B are shown in Table II. The yields were a little lower than for procedure A, being around or slightly

TABLE II

DETERMINATIONS WITH PROCEDURE B

25 g of human liver were used for each analysis

Liver	*Added*			*Thallium, µg*		*Recovery* %
	Tl µg	*ion*	*mg*	*Found*	*Blank*	
G	10			8	0	80
G	40			35	0	87.5
F	100			99	0	99
F	200			191	0	95.5
F	0	Hg^{II}	100	−2	0	
G	20	Hg^{II}	100	18	0	90
F	100	Hg^{II}	100	100	0	100
G	200	Hg^{II}	100	196	0	98
F	300	Hg^{II}	100	303	0	101
F	200	Cd^{II}	100	237	0	118.5
F	200	Cd^{II}	50	218	0	109
F	200	Bi^{III}	100	219	0	109.5
G	200	In^{III}	100	203	0	101.5

below 100%. At the lowest thallium content, less than 50 µg, the yields dropped to 80–90%. The low blank values, 0 µg for two different liver samples, made it possible to determine a smaller thallium content with procedure B than with procedure A; 10 µg in liver samples could be analysed, qualitatively and quantitatively, with reasonable accuracy.

The influence of the four metals which interfered in procedure A was studied, especially that of mercury (Table II); it was found that mercury (100 mg) and indium (100 mg) did not affect the determination whereas bismuth (100 mg) and cadmium (50 mg) interfered only slightly.

SUMMARY

Two variations of a method for the determination of microgram amounts of thallium in biological material have been worked out. After wet combustion and separation of thallium from most interfering substances by extraction of thallic chloride with ether, the metal is estimated absorptiometrically as its dithizonate, the yield being slightly greater than theoretical (procedure A). In the presence of mercury (> 1 mg), cadmium, bismuth and indium (> 10 mg) high results were obtained. Other metals, halogen, thiosulphate and thiocyanate ions did not interfere. With the slightly longer procedure B, serious interference was not encountered from any metal in amounts up to 50 mg. For practical purposes procedure B can be considered specific for thallium. As little as 10 µg of thallium in 25 g of liver could be determined.

RÉSUMÉ

Deux variantes sont proposées pour le dosage du thallium dans des substances biologiques. Après minéralisation et extraction, le thallium est dosé absorptiométriquement sous forme de dithizonate. L'un de ces procédés est moins rapide que l'autre; mais il peut être considéré pratiquement comme spécifique.

ZUSAMMENFASSUNG

Es werden zwei Varianten einer Methode beschrieben zur Bestimmung von Thallium in biologischem Material. Nach Zerstörung der organischen Substanz wird das Thallium als Chlorid extrahiert und als Dithizonat absorptiometrisch bestimmt. Die eine Variante benötigt etwas mehr Zeitaufwand, kann aber als spezifisch betrachtet werden.

References p. 365

REFERENCES

[1] H. OSTEN, *Führer-Wieland's Samml. Vergiftungsfällen*, 11, Abt. C (1940) 55.
[2] J. R. A. ANDERSON, *Anal. Chem.*, 25 (1953) 108.
[3] E. B. SANDELL, *Colorimetric determination of traces of metals*, 3rd Ed., Interscience Publishers, Inc., New York 1959.
[4] G. IWANTSCHEFF, *Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse*, Verlag Chemie, G.m.b.H., Weinheim 1958.
[5] K. BAMBACH, *Ind. Eng. Chem., Anal. Ed.*, 12 (1940) 63.
[6] P. A. E. KAMERMAN, *J. S. African Chem. Inst.*, 27 (1944) 22.
[7] R. S. CLARKE, JR., AND F. CUTTITTA, *Anal. Chim. Acta*, 19 (1958) 555.
[8] H. FISCHER, *Angew. Chem.*, 50 (1937) 919.
[9] J. F. REITH AND K. W. GERRITSMA, *Rec. trav. chim.*, 65 (1946) 770.
[10] H. M. IRVING AND F. J. C. ROSSOTTI, *Analyst*, 77 (1952) 801.
[11] A. K. KLEIN, *J. Assoc. Offic. Agr. Chemists*, 35 (1952) 537.
[12] H. WANNTORP AND A. DYFVERMAN, *Arkiv Kemi*, 9 (1956) 7.
[13] J. ANDREWS AND W. J. STRINGER, *J. Inst. Brewing*, 57 (1951) 363.

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MULTIPURPOSE ELECTROANALYTICAL INSTRUMENT INCORPORATING AN X-Y RECORDER

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The basic quantities measured in electroanalytical chemistry are current, potential, and time. Measurement or recording of various combinations of these quantities accounts for most electroanalytical methods:

1. Current *vs.* potential, (a) voltammetry at constant potential, (*e.g.* polarography), (b) voltammetry at continuously changing potential, (c) current-electrode potential curves with macro-electrodes.

2. Potential *vs.* time, (a) chronopotentiometry, (b) potentiometric titration curves, involving coulometric generation or constant addition of titrant.

3. Current *vs.* time, (a) chronoamperometry, (b) amperometric titration curves, coulometric generation or constant addition of titrant.

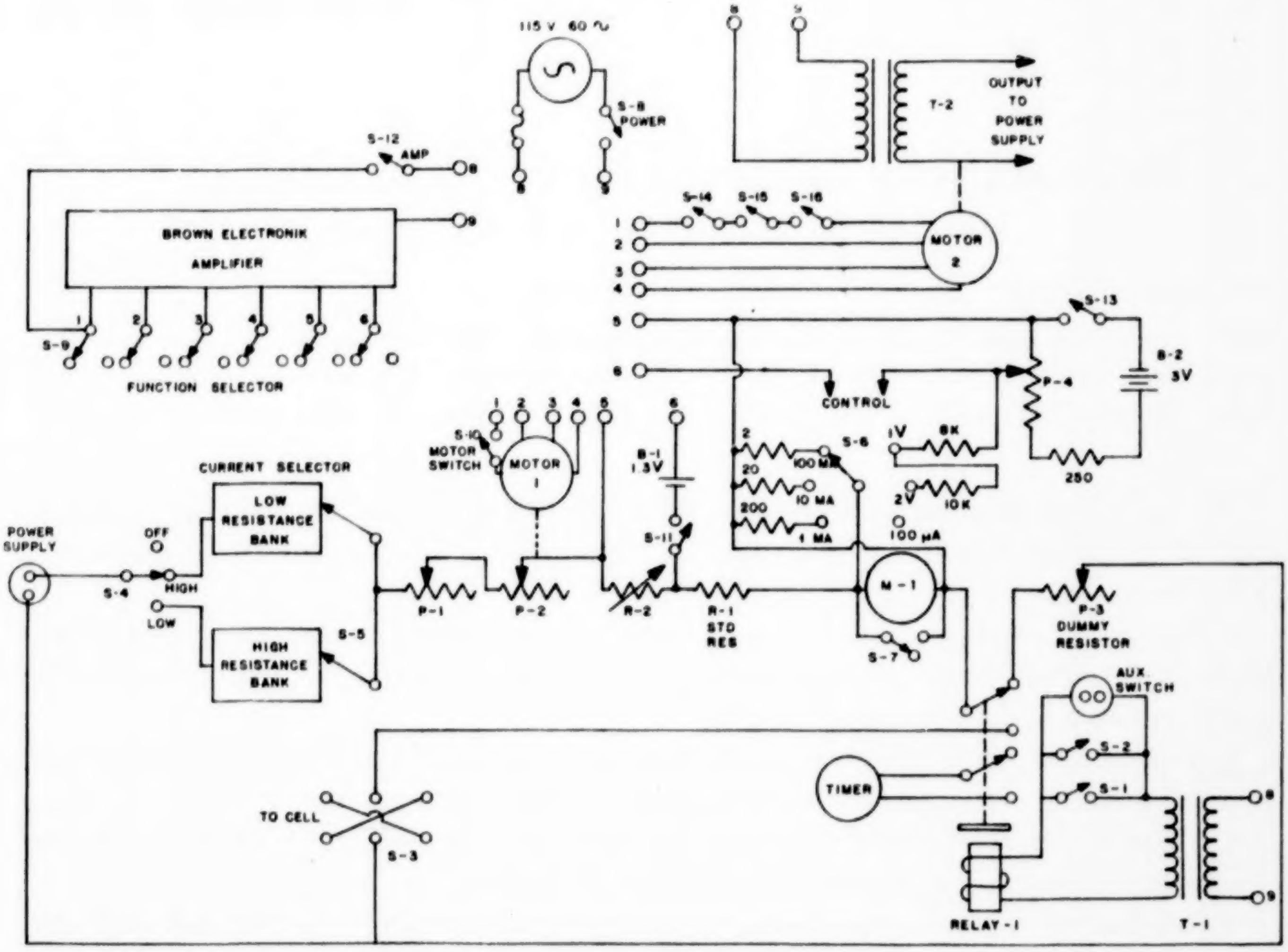
Recording of current or potential *vs.* time is generally easily performed with galvanometer or "continuous-balance" strip chart recorders. The recording of current *vs.* potential, however, involves synchronizing the chart drive of the recorder with the polarizing unit drive. Since cell voltage, rather than electrode potential, is being recorded, the polarization curve inevitably includes the *iR* drop of the circuit. Although this *iR* drop generally does not cause serious error in the measured potentials when the cell resistance and current are small (*e.g.* polarography), attempts to record large currents (up to 100 mA) *vs.* potential, for example for use in predicting current efficiencies in coulometric titrations, are doomed to failure.

The direct recording of current-potential curves, as pointed out by LINGANE[1], could be accomplished with an X-Y recorder (or "function plotter"), recording the e.m.f. between the working electrode and a reference electrode on one axis, and the current flowing between the working electrode and an auxiliary electrode on the other axis. A polarograph utilizing this principle for accurate measurement of half-wave potentials and polarography in high resistance media has recently been described[2].

The present paper describes the application of an X-Y recorder, with a built-in time base, for all types of electroanalytical measurements. The instrument includes a variable polarizing source, for potential (or current) sweeps of 8 sec to 80 min, and an electromechanical amperostat–potentiostat combination for application to coulometry and controlled potential separations.

APPARATUS

The amperostat–potentiostat was essentially a combined version of the Lingane amperostat[3] and the Lamphere-Rogers potentiostat[4], utilizing the same amplifier for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FUNCTION SELECTOR
S-14
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S-16
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MOTOR
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S-13
B-2
3V
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CONTROL
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S-10
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SWITCH
MOTOR
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B-1
1.3V
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2
20
200
100 MA
10 MA
1 MA
S-6
1V
8K
2V
10K
100 μA
250
CURRENT SELECTOR
LOW
RESISTANCE
BANK
HIGH
RESISTANCE
BANK
S-5
POWER
SUPPLY
OFF
HIGH
LOW
S-4
P-1
P-2
R-2
R-1
STD
RES
M-1
S-7
P-3
DUMMY
RESISTOR
AUX.
SWITCH
S-2
S-1
TIMER
TO CELL
S-3
RELAY-1
T-1
8
9

Fig. 1. Amperostat–potentiostat circuit:

M-1 = Microammeter (0–100 μA. d.c.; Simpson Panel Meter Model 29), relay-1 = Advance relay, Type AH/2C1C, T-1 = Power transformer (Merit P-2944), T-12 = General Radio Company Type V-10 Variac autotransformer (0–135 V. 10 A), P-1 = Borg micropot. Model 205, 10-turn, 0.1% linearity, P-2 = Potentiometer (General Radio Co. Type 974), P-3 = 500 Ohm potentiometer, P-4 = 500 Ohm potentiometer (General Radio Co. Type 975-J), R-1 = Precision resistor (General Radio Co. Type 500), R-2 = Decade resistor (General Radio Co. Type 1432 N), B-1 = 1.3 V mercury battery, B-2 = 3.0 V dry battery, S-1, S-7, S-10, S-11, S-12, S-13, S-14 = S.p.s.t. switches, S-2 = Microswitch, S-3 = D.p.d.t. switch, S-4 = 3-position, single pole switch (Centralab 1472), S-5 = 11-position, double pole switch (Centralab 2513), S-6 = 6-position, single pole switch (Centralab PA 2043), S-9 = 2-position, 6 pole switch (Centralab PA 2019), S-15, S-16 = Limit switches, Microswitch, leaf-action type, amplifier = Brown electronik model 356410-1, 115 V. 60 cycle. Motor 1 = Brown servo motor 364949, 115 V. 22 r.p.m., Motor 2 = Brown servo motor 364949, 115 V. 22 r.p.m., (1 : 40 reduction gear drive to T-2).

both instruments. A schematic diagram of the circuit is shown in Fig. 1. The device is easily assembled from commercially available components, and requires little skill in electronic circuitry. The use of an electromechanical device allows currents of from 1 μA to 100 mA, by changing only the series resistances P-1 and P-2 and adjustment of R-2. The principle of operation of this instrument is discussed in detail in the literature[1,3,4]. The unit described has the advantage of versatility and reduction in cost by use of a common chopper-amplifier system for both functions.

A Moseley Model 3S X-Y recorder (F. L. Moseley Co., Pasadena, Calif.), with a built-in time base was employed throughout. This is a flat-bed recorder, utilizing standard 81/2 by 11 inch graph paper as a recording medium. Employed as an X-Y recorder, voltage input to either axis is continuously variable from 5 mV to 500 V. The time base (incorporated on the X-axis) allows full-scale sweep times of from 5 to 500 sec. Each scale may be calibrated, with an accuracy of 0.1%; changes in accuracy accruing to no more than 0.25% over a 6 month period. Both axis have identical response, and require 1/2 sec for full-scale pen travel.

Potential input

Direct input to the recorder for measurement of electrode potential is usually undesirable, as sizeable current drain through the recorder input attenuator, and consequently *iR* drop, occurs. Potential input with negligible current drain may be obtained by several devices. The X-axis of the recorder may be modified to make it a 1 V, zero current potentiometric system[2], but this has the distinct disadvantage of allowing only one potentiometric voltage range to be used. An alternate method is to employ a preamplifier in the potential input. The versatile pH meter Model 7664 (Leeds and Northrup Co., Philadelphia, Pa.) was quite suitable for this purpose. The recorder output of the meter was connected to the X-Y recorder, with the axis set for 20 mV full scale. The input to the pH meter consisted of voltage ranges of 0 to 700 mV and 0 to 1400 mV with the zero positioned anywhere on the scale. Other voltage ranges may be obtained by putting a variable resistance across the temperature compensation input of the pH meter (80–100 Ohms per 100 mV full scale deflection). Advantages of the pH meter input are the ability for use with very high input impedances (up to 2000 megOhms) for use with glass electrode measurements or high resistance voltammetry, and the ease with which orientation of the recorder scale can be accomplished. Accuracy is limited to that of the pH meter, but careful calibration provides sufficient accuracy for most electroanalytical measurements.

Current input

Current measurements are conveniently made by measuring the *iR* drop over precision resistors. Employing the 5 mV input to the recorder, current measurements of 0.1 μA to 1 mA is performed using 50,000 to 5 Ohm resistors. Higher currents may be measured using higher voltage inputs. The measuring resistors employed were either a decade box (*e.g.* Type 1432, General Radio Co., Cambridge, Mass.) or plug-in precision resistors (General Radio Co. Type 500).

Time input

The Moseley Model 3S is equipped with a built-in (charging capacitor-type) time base, providing 5 to 500 sec full scale sweeps. The linearity and reproducibility of this time base was good. For longer time sweeps, or for X-Y recorders not including time bases, a ten-turn precision helipot driven by a synchronous motor can be used.

Polarizing unit

The polarizing unit was a motor-driven infinitely variable, reversible speed reducer, Zeromax Model M14R (Revco, Inc., Minneapolis, Minn.) driving (through a 1 : 100 gear reduction) either an autotransformer (Variac Type W2, General Radio Co.,) or a helipot. This unit has the capability of voltage or current sweeps of 8 sec to 80 min, with any desired current (up to 2 A) or voltage range. Generally, the autotransformer was connected to 120 V.A.C. and was used as a source for a selenium rectifier power supply (*e.g.* General Radio Co. Type 1204 B). Alternately the usual bridge voltage sources were employed[2,5]. The reversibility of the motor allows scans to be made in either direction. Limit switches were included at both ends of the scanning range to protect the autotransformer and automatically turn off the apparatus. Since the recorder plots potential directly, usual considerations of slide wire linearity and motor speed constancy were unnecessary. However, the scan voltage circuit employed was sufficiently linear and constant for use in voltammetry with continuously rapid changing potential.

APPLICATIONS

Amperostat

The use as a constant current source has been described[3]. One need only select the current desired and adjust for balance and current constant to at least ± 0.1% can be obtained for use in coulometric titrations or chronopotentiometry.

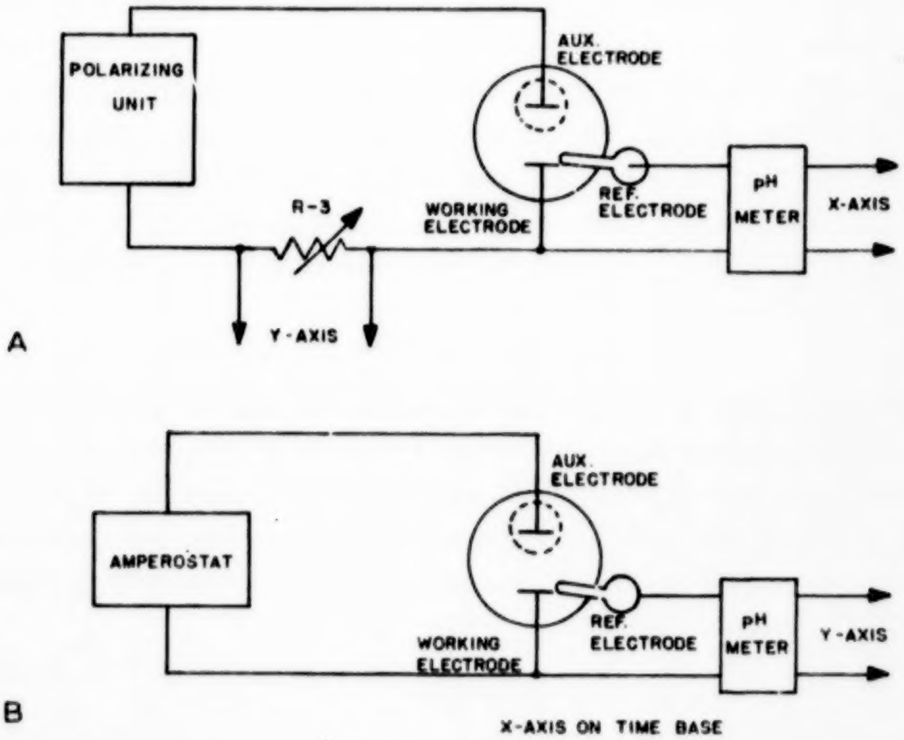

Fig. 2. A. Circuit for current-potential curves, B. Circuit for chronopotentiometry.

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Potentiostat

For use as a potentiostat, the function switch S-9 is turned to potentiostat, and the potential desired is adjusted with P-4 observing the meter (at 1 or 2 V range). Input to the autotransformer T-2 is 120 V.A.C. and the output voltage is fed to any selenium rectifier power supply. A potential of 1 V was maintained constant to within 10 mV as cell resistance varied from 500 to 1,000 Ohms in 5 min.

Current-potential curves

The set-up for any type of current-electrode potential measurement is shown in Fig. 2A. Adjustment of the variable precision resistor R-3 fixes the current range, and the total polarizing voltage and selected input to the pH meter selects the voltage range. This basic apparatus was employed for polarography (either voltage–scan or current–scan) or current–potential curves with macro-electrodes.

Chronopotentiometry

The apparatus for chronopotentiometry is shown in Fig. 2B. Current–time (chronoamperometric) curves are recorded in a similar manner, using a current input to the Y-axis. In a similar manner both potentiometric and amperometric titration curves of various types can be recorded, using separate indicator electrodes.

The unit described has proved both versatile and convenient. The total cost of the complete instrument, including the amperostat–potentiostat, pH meter and recorder was approximately $ 2,500.

SUMMARY

A multipurpose electroanalytical instrument, incorporating an X-Y recorder with a built-in time base, is described. The instrument also includes an electro-mechanical combination amperostat–potentiostat and a variable speed polarizing unit. The instrument accurately measures electrode potential (rather than cell voltage) and hence does not involve correction of recorded potentials for *iR* drop. This is especially convenient for the recording of current *vs.* potential curves with macroelectrodes. It has also been successfully used for voltammetry, chronopotentiometry, coulometry and recording of titration curves.

RÉSUMÉ

Un appareil électroanalytique à usages multiples est décrit. Il convient tout particulièrement pour l'enregistrement de courbes potentiel/courant, avec macro-électrodes. Il a également été utilisé avec succès pour la voltammétrie, la chronopotentiométrie, la coulométrie et l'enregistrement de courbes de titrage.

ZUSAMMENFASSUNG

Es wird ein elektranalytisches Mehrzweck-Gerät beschrieben, das sich besonders zur Aufnahme von Potential-Stromstärke Kurven mit Makroelektroden eignet. Ferner lässt es sich für die Voltametrie, Chronopotentiometrie, Coulometrie sowie zur Aufnahme von Titrationskurven verwenden.

REFERENCES

[1] J. J. LINGANE, *Electroanalytical Chemistry*, Interscience Publishers, New York 1958.

[2] D. T. SAWYER, R. L. PECSOK AND K. K. JENSON, *Anal. Chem.*, 30 (1958) 481.

[3] J. J. LINGANE, *Anal. Chem.*, 26 (1954) 1021.

[4] R. W. LAMPHERE AND L. B. ROGERS, *Anal. Chem.*, 22 (1950) 463.

[5] I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Interscience Publishers, New York 1952, p. 307.

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SPECTROPHOTOMETRIC DETERMINATION OF GERMANIUM WITH 1,1'-DIANTHRIMIDE

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INTRODUCTION

During an investigation of the elements interfering in the spectrophotometric determination of boron with 1,1'-dianthrimide, it was observed that germanium also produced a colour with this organic reagent. The reactions of boron and germanium with 1,1'-dianthrimide take place in concentrated sulfuric acid, and the colours are developed by heating. In the literature no reference is made to the use of 1,1'-dianthrimide for the detection or determination of germanium.

The present paper describes the application of 1,1'-dianthrimide for spectrophotometric determination of germanium.

INSTRUMENTS AND REAGENTS

Instruments

Extinction measurements were made with a Zeiss spectrophotometer PMQ II. A matched set of 1,000-cm glass cells was used.

Reagents

The spectrographically standardized germanium dioxide (Johnson, Matthey & Co.) contained the following amounts of impurities: silicon — 3 p.p.m., silver — 1 p.p.m., copper, calcium, and magnesium <1 p.p.m., arsenic <0.05 p.p.m.

The 1,1'-dianthrimide (E. Merck) was recrystallised twice from nitrobenzene before use.

Concentrated sulfuric acid (95–97%) and other chemicals were of reagent grade quality. The strength of the sulfuric acid used was found to be 96.8%. Precautions were taken to prevent the acid absorbing water vapour.

Ordinary distilled water from an all-metal still was used.

Glassware

The germanium 1,1'-dianthrimide solutions were prepared and heated in 50-ml bottles (Jena geräteglass) with ground-in glass stoppers.

Heat treatment

The solutions were heated in a thermostatically controlled drying oven of standard construction.

EXPERIMENTAL DATA

Standard solutions

Germanium dioxide (0.1440 g) was dissolved in 50 ml of 1% sodium hydroxide solution. After dilution to 100 ml the germanium solution was stored in a plastic bottle. The standard solution contained 1 mg germanium per ml. A blank solution containing the same amount of sodium hydroxide was prepared, diluted to 100 ml and stored in a plastic bottle.

1,1'-Dianthrimide (0.500 g) was dissolved in conc. sulfuric acid, and the solution was transferred to a 1000-ml volumetric flask and diluted to the mark with the same acid.

Absorption curves

In Fig. 1, Curve 1, an absorption curve of the germanium 1,1'-dianthrimide complex is plotted. Curve 2 (Fig. 1) shows the absorption curve of a solution of 1,1'-dianthrimide.

The solutions measured photometrically were prepared in the following way. For curve 1, 1 ml of germanium standard solution, 12 ml of conc. sulfuric acid, and 5 ml of 1,1'-dianthrimide standard solution were pipetted into a 50-ml bottle. The bottle was stoppered, and the solution mixed and then kept in the oven for 16 h at 70° ± 2°. The solution was then cooled to room temperature and the extinction at different wavelengths measured against a blank solution consisting of 1 ml of the sodium hydroxide solution, 12 ml of conc. sulfuric acid, and 5 ml of 1,1'-dianthrimide standard solution. Curve 2 is the absorption curve of this latter solution measured against conc. sulfuric acid.

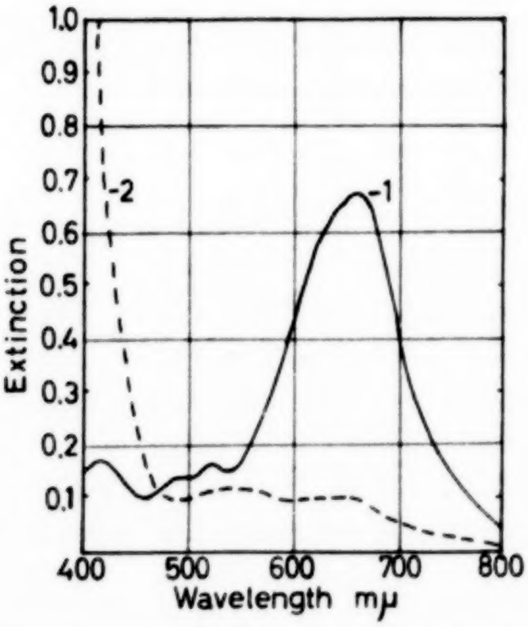

Fig. 1. Curve 1: Absorption curve of the germanium 1,1'-dianthrimide complex. Curve 2: Absorption curve of 1,1'-dianthrimide.

The absorption curve of the germanium 1,1'-dianthrimide complex shows a distinct maximum at 660 mμ. This wavelength was chosen for the determination of germanium.

It is interesting to note that the form of the absorption curve of the boron 1,1'-dianthrimide complex in sulfuric acid of the same strength is nearly identical to curve 1 in the figure given above.

Calibration curve

The validity of the Beer-Lambert law was tested by measuring the extinction of a series of solutions containing varying known amounts of germanium. Into a series of 50-ml bottles were pipetted 0.2, 0.4, 0.5, 0.6, 0.7, 0.8 and 1.0 ml of germanium standard solution. Volumes of less than 1 ml were diluted to that volume with the blank solution containing sodium hydroxide. Then 12 ml of conc. sulfuric acid and 5 ml of 1,1′-dianthrimide standard solution were added to each bottle, and the solutions were heated for 16 h at 70° ± 2°. The extinctions were measured against a blank prepared and treated in the same way.

Owing to contraction the volume of these solutions was not 18.0, but 17.6 ml.

TABLE I

EXTINCTION DATA FOR THE DETERMINATION OF GERMANIUM WITH 1,1′-DIANTHRIMIDE
WAVELENGTH 660 $m\mu$

Mg Ge per 17.6 ml (C)	*Extinction (E)*	*Extinction index (E/C)*
0.2	0.146	0.730
0.4	0.289	0.723
0.5	0.362	0.724
0.6	0.427	0.712
0.7	0.488	0.697
0.8	0.550	0.688
1.0	0.679	0.679

From Table I it is seen that a negative deviation from the Beer-Lambert law was obtained within the concentration range examined.

Effect of temperature

The colour of the germanium 1,1′-dianthrimide complex was developed by heating, and a temperature of 70° was chosen.

The effect of higher temperatures on the colour development was investigated. When heating was carried out at 80° or higher, the extinction of the solutions was less than that of solutions heated at 70°. At higher temperatures a red colour appeared in addition to the bluish-green colour of the germanium 1,1′-dianthrimide complex; the red colour probably originated from a decomposition product of 1,1′-dianthrimide. Consequently, a temperature above 70° cannot be recommended.

Effect of heating time

A relatively long heating time was needed to obtain equilibrium conditions. In this investigation a time of 16 h at 70° was used. Prolonged heating resulted in a decrease of extinction, probably again owing to destruction of the reagent.

Effect of concentration of sulfuric acid

The effect of the concentration of acid on the development of the colour was investigated for solutions heated for 16 h at 70°.

A series of solutions was prepared in which the concentrations of germanium and 1,1′-dianthrimide were kept constant, while the concentration of sulfuric acid was varied. The extinction of the solutions was measured against a series of blank solutions containing the same amounts of 1,1′-dianthrimide and sulfuric acid as the corresponding sample solution. The extinction of the blank solutions was measured against conc. sulfuric acid. The extinction data obtained are given in Table II.

TABLE II

EFFECT OF CONCENTRATION OF SULFURIC ACID. CONCENTRATION OF UNDILUTED H_2SO_4 96.8%. ALL SOLUTIONS CONTAINED 1 mg Ge AND 2.5 mg 1,1'-DIANTHRIMIDE. WAVELENGTH 660 *mμ*

ml H_2O taken	*ml H_2SO_4 (96.8%) taken*	*Conc. of H_2SO_4 after dilution %*	*Extinction*	
			Sample sol. against blank	*Blank sol. against H_2SO_4 96.8%*
1.0	19.0	94.1	0.639	0.099
1.5	18.5	92.7	0.474	0.091
2.0	18.0	91.3	0.350	0.083
2.5	17.5	89.8	0.251	0.076
3.0	17.0	88.3	0.181	0.070
3.5	16.5	86.8	0.123	0.063
4.0	16.0	85.2	0.080	0.056

It is seen from Table II that the concentration of sulfuric acid is very critical. The extinction decreased rapidly when the acid was diluted. Further dilution resulted in the precipitation of 1,1'-dianthrimide.

Influence of foreign ions

The effect of foreign ions on the extinction of solutions of the germanium 1,1'-dianthrimide complex was not investigated, but on the basis of unpublished work on the influence of foreign ions in the determination of boron with 1,1'-dianthrimide, it is possible to obtain information about the ions interfering in the determination of germanium.

When the extinction of solutions of the germanium 1,1'-dianthrimide complex is about 0.5, the following ions affect this value by less than ± 3% (the concentrations of the different ions are given in brackets in mg per 17.6 ml):

Ag^+(2); Al^{+3}(5); Ba^{+2}(50); Bi^{+3}(1); Ca^{+2}(100); Cd^{+2}(50); Co^{+2}(20); Cr^{+3}(10); Cu^{+2}(20); Fe^{+2}(20); K^+(20); Li^+(10); Mg^{+2}(20); Mn^{+2}(10); Na^+(130); Ni^{+2}(20); Pb^{+2}(1); Si^{+4}(1); Sn^{+2}(20); Ti^{+4}(1); Tl^+(10); Zn^{+2}(50); Cl^-(200); $Cr_2O_7^{-2}$(0.01); F^-(0.01); PO_4^{-3}(100) and SO_4^{-2}(138).

The following ions interfere: B^{+3} in all concentrations, Br^- (oxidized in conc. sulfuric acid) and F^- in concentrations above 0.01 mg per 17.6 ml. Interference from fluoride ions is probably due to attack on glass and release of boron.

DISCUSSION

The authors have determined the formula of the complex between germanium and 1,1'-dianthrimide and have found it to be a 1 : 1 complex. From the data given in the present paper, it is clear that the ligand (1,1'-dianthrimide) was not added in excess compared with the amounts of germanium present. An excess was not used because of the high absorption of the 1,1'-dianthrimide blank solutions.

Even in the presence of insufficient 1,1'-dianthrimide Beer-Lambert's law was followed with only a slight negative deviation. It therefore seems clear that only a fraction of the amount of germanium present reacts with 1,1'-dianthrimide. Within the concentration range examined this fraction seems to be independent of the concentration of germanium. The amount of germanium reacting with 1,1'-dianthrimide was calculated to be of the order of 10% of the total amount present.

SUMMARY

In conc. sulfuric acid a coloured complex is formed between germanium and 1,1'-dianthrimide, which has an absorption maximum at 660 mμ, and can be used for the spectrophotometric determination of germanium. The method is applicable at concentrations up to at least 6 mg Ge per 100 ml. Among the more common ions serious interference is caused by boron and fluoride. The interference from fluoride is probably due to attack on the glass and release of boron.

RÉSUMÉ

En milieu acide sulfurique concentré la 1,1'-dianthrimide donne avec le germanium un complexe coloré, ayant un maximum d'absorption à 660 mμ. Une méthode est proposée pour le dosage spectrophotométrique du germanium au moyen de ce réactif.

ZUSAMMENFASSUNG

Germanium bildet mit 1,1'-Dianthrimid in conc. Schwefelsäure einen gefärbten Komplex, der sich zur spektrophotometrischen Bestimmung des Germaniums eignet; Absorptionsmaximum bei 660 mμ.

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AN EVALUATION OF SOME SIMPLE SULFONIC ACIDS AS NONAQUEOUS TITRANTS*

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Although the sulfonic acids have been proved to be strong acids in a glacial acetic acid medium, they have not been widely investigated as titrants for use in nonaqueous titrimetry. HAMMETT AND DIETZ[1] dissolved benzenesulfonic acid in formic acid and used this titrant for the determination of bases in a potentiometric study of various acid–base titration systems. SMITH AND ELLIOTT[2], in an investigation of acid strengths and dissociation constants, found that methanetrisulfonic, chloromethionic, and methionic acids were stronger acids than perchloric acid. Since no information is available concerning the simpler sulfonic acids, methane- and ethane- in the aliphatic group and no further information on the aromatic benzene- and naphthalene-, this study sought to ascertain their analytical possibilities.

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From the viewpoint of nonaqueous theory the sulfonic acids are interesting since the presence of the sulfonic acid group implies strong acid properties. By electron shifts the sulfur atom acquires a doubly positive charge and the resulting anion is stabilized by resonance. Since the proton is less firmly held, the O–H bond is weakened and greater acidity can be anticipated.

The choice of solvent system for the sulfonic acids provided the first problem. HAMMETT AND DIETZ[1] used formic acid as a solvent for their study reporting that they found this medium freer from salt effects. However, formic acid is less stable and more difficult to obtain in an anhydrous form than acetic acid, so it was decided to use the latter and more common system basing this selection on the following points:
(1) The reagent grade chemical, as obtained from the manufacturer, was pure and could be easily freed from water by treatment with acetic anhydride.
(2) The simple sulfonic acids to be used in the study were soluble in this medium.
(3) For potentiometric titrations the glass-calomel electrode system gave steady and reproducible readings in this solvent. Equilibrium was achieved quickly after the addition of each increment of titrant.
(4) During the titration with this solvent, the system remained free from the formation of precipitates or gels, so likely to occur in any anhydrous titration.

EXPERIMENTAL

Apparatus

Potentiometric titrations were performed with a Shell-Precision Titrometer equipped with a sleeve-type calomel electrode and a glass electrode. The titration assembly consisted of a 150-ml tall-form beaker, covered with a plastic lid. Three openings in the lid admitted the electrodes and buret tip into the titration beaker. The titrant was delivered from a 10-ml buret calibrated at 25° in the normal way. A magnetic stirrer and a glass-covered stirring bar were used to stir the solution during the titration.

Reagents and chemicals

Potassium acid phthalate (primary standard grade, Merck), was dried at 145° for 3h.
Glacial acetic acid, C. P. (Baker).
Methanesulfonic acid (reagent grade, Eastman).
Ethanemonosulfonic acid (reagent grade, Brothers Chemical).
Benzenesulfonic and naphthalene-2-sulfonic acids (reagent grades, Eastman).

Preparation of titrants

Methanesulfonic acid was found by aqueous assay to have a purity of 95.5%, the remaining 4.5% probably water. No opalescence was produced with barium chloride. Since the aliphatic sulfonic acids exhibited supercooling, the acid had to be cooled below 20°, its freezing point. It was found to solidify at 16°. Upon cooling, the acid became quite viscous, another characteristic of the entire series. It was purified by repeated fractional crystallizations, according to the method of BERTHOUD[3].

A 0.1 *N* solution of methanesulfonic acid was made up by dissolving 6.80 ml of the purified acid in a liter of glacial acetic acid, adding acetic anhydride to react with the trace of water present[4]. Methanesulfonic acid was found to dissolve readily and remain in solution for the entire period during which it was used.

Ethanemonosulfonic acid gave an aqueous assay of 98.5% purity. The product was purified by fractional crystallization according to the method of BERTHOUD[3]. It exhibited characteristics similar to the methane member of the series and had a freezing point of —17°. A 0.1 *N* solution of this acid was prepared by dissolving 8.80 ml of the purified product in one liter of glacial acetic acid and adding acetic anhydride to react with any trace of water still remaining.

Benzenesulfonic acid was recrystallized several times from acetic acid and dried in a vacuum desiccator for over a week before use. In order to facilitate drying, the crystals were finely crushed and spread over a large surface. Due to its hygroscopic character, the material could not be weighed accurately. About 1.6 g were added to 100 ml of glacial acetic acid, acetic anhydride added to remove traces of water, and the resulting solution was permitted to stand at least overnight to insure the completion of the reaction of the anhydride with the water present. It was then titrated to determine its concentration and, subsequently, diluted to the desired normality.

Naphthalene-2-sulfonic acid gave no opalescence with barium chloride and showed the presence of a trace of water. It was recrystallized from acetic acid and dried by the same method as was used for benzenesulfonic acid above. About 2.3 g were dissolved in 100 ml acetic acid, and acetic anhydride added, to make a 0.1 *N* solution. The crystals did not appear to pick up water to any considerable extent during the weighings.

Procedure

Exactly 0.1635 g of potassium acid phthalate was weighed into tall form beakers and 10.0 ml of glacial acetic acid added to dissolve the sample. In order to completely dissolve the solid, it was necessary to heat the solution gently for 3 min. The solution was then cooled and titrated potentiometrically with a 0.1 *N* solution of each of the aliphatic and aromatic sulfonic acids.

Standard solutions of potassium acid phthalate were also prepared and aliquot portions titrated with the same apparatus as mentioned above. A few drops of crystal violet indicator solution in acetic acid were added to check the sharpness of the color change at the potentiometric end-point. For all titrations, the glass–calomel electrode system was used.

RESULTS

A series of 9 to 10 titrations for each acid were evaluated statistically from potentiometric data, as seen in Table I, on the basis of the height of the potential break and the maximum value of dE/dV, the rate of change of potential with volume of titrant. For a fair test of the analytical possibilities of the acids as new acidic titrants, it was thought advisable to make a comparison with perchloric acid in the same solvent. The results of this test, also listed in Table I, show the greater acid strength of perchloric acid. It is interesting to note, however, that in the course of this work with the sulfonic

TABLE I

COMPARISON OF ACID STRENGTHS OF 0.1 N SOLUTIONS OF SULFONIC ACIDS AND PERCHLORIC ACID FROM POTENTIOMETRIC DATA

Acid	*Determinations*	*Maximum dE/dV*	*Potential break, mV*
CH_3SO_3H	9	497	220
$C_2H_5SO_3H$	10	436	200
$C_6H_5SO_3H$	9	542	240
$C_{10}H_7SO_3H$	10	540	234
$HClO_4$	10	1300	315

acids, it became increasingly evident that precipitates or gels are not formed during the titrations. These precipitates, reported extensively in the literature and confirmed in this work, are repeatedly obtained when perchloric acid is used as the titrant.[5]

The titration curves for the sulfonic acids, as illustrated in Figs. 1 and 2, are characteristic of strong acids from a consideration of both their shape and their large potential break at the end-points. Sharp color responses could be expected from indicators and

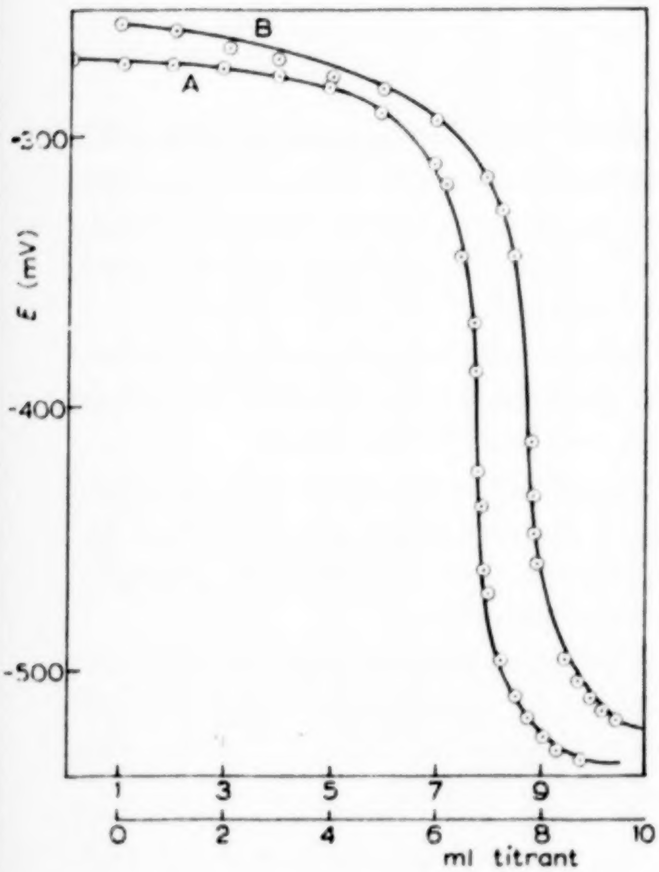

Fig. 1. Standardization of aliphatic sulfonic acids with potassium acid phthalate. Solvent: glacial acetic acid; electrode system: glass–calomel; standard: 0.80 mequivs. potassium acid phthalate; titrants: 0.1 N solutions of: A, methanesulfonic acid; B, ethanemonosulfonic acid.

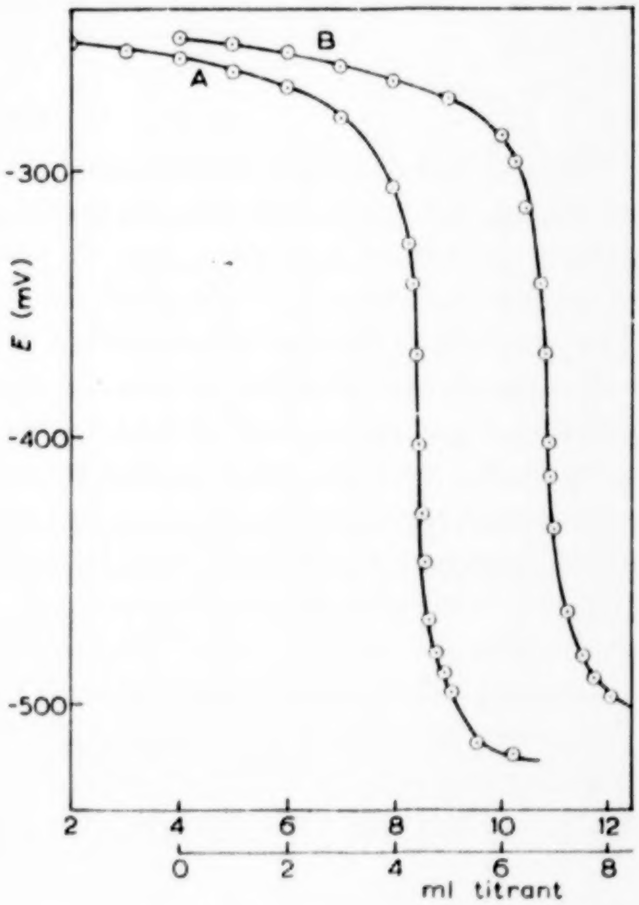

Fig. 2. Standardization of aromatic sulfonic acids with potassium acid phthalate. Solvent: glacial acetic acid; electrode system: glass–calomel; standard: 0.80 mequivs. potassium acid phthalate; titrants: 0.1 N solutions of: A, benzenesulfonic acid; B, naphthalenesulfonic acid.

TABLE II

PRECISION OF THE ALIPHATIC AND AROMATIC SULFONIC ACIDS STANDARDIZED *vs.* POTASSIUM ACID PHTHALATE

Acid titrant	*Determinations*	*Normality*	*Standard deviation parts/1000*
CH_3SO_3H	10	0.1014	0.00017
$C_2H_5SO_3H$	10	0.1017	0.00028
$C_6H_5SO_3H$	10	0.1059	0.00049
$C_{10}H_7SO_3H$	10	0.1010	0.00040

crystal violet was added to the titration solution to check its response. The color change at the end-point was sufficiently sharp as to suggest the possibility of visual titrations for the standardization. However, in the use of any indicator in nonaqueous work, it is advisable to check the color change at the potentiometric end-point first since a great variation has been found for different substances[6].

From the sharp potential break at the end-point in the standardization of these acids, good precision can be anticipated. Table II lists the precision found in the standardization against potassium acid phthalate. The precision is of the order of 0.2 to 0.5 % which is excellent for nonaqueous titrations.

DISCUSSION

The method described here illustrates the simplicity of preparing some sulfonic acids as nonaqueous titrants in a glacial acetic acid medium. These acids can be standardized against potassium acid phthalate by potentiometric measurements. Reproducibility of results was found to be excellent when the glass-calomel electrode system was used. The precision of the method was of the order of 0.2 to 0.5%.

For the standardization process it is also possible to use aliquot portions of a standard solution of potassium acid phthalate dissolved in acetic acid. This solution was found to be stable over the entire period during which it was used in this work.

Although none of the sulfonic acids tested were as strong as perchloric acid, they had an advantage over the latter in so far as they did not produce gels or precipitates in the titration with potassium acid phthalate. A complete study of precipitation formation in the titration of other basic substances is now in preparation.

Although the aromatic sulfonic acids tested showed less precision than the aliphatic, they likewise titrated as strong acids. The handling of naphthalene-2-sulfonic acid proved much simpler than that of benzenesulfonic acid, since the difficulty of removing water and working with a hygroscopic compound was not present.

SUMMARY

The simple aliphatic and aromatic sulfonic acids show evidence of possibilities as new titrants in a glacial acetic acid medium. Excellent precision is obtained in potentiometric titrations with both ethane- and methane sulfonic acids with a standard deviation of 0.2%. Benzenemonosulfonic and naphthalenesulfonic acids both give an average precision of 0.4%. In visual titrations with with crystal violet indicator, the color changes at the end-point are very sharp. The chief advantage of these acids as titrants lies in the fact that they dissolve readily in glacial acetic acid and can be titrated to give reproducible results with the glass–calomel electrode system. None of the sulfonic acids tested was as strong a titrant as perchloric acid, but, unlike perchloric acid, they did not form precipitates or gels in the titration with potassium acid phthalate.

RÉSUMÉ

Les auteurs proposent l'emploi d'acides aliphatiques et aromatiques sulfoniques pour des titrages en milieu non aqueux. Les acides méthanesulfonique et éthanesulfonique, en particulier, permettent d'obtenir une très bonne précision. Ces acides présentent l'avantage de se dissoudre très facilement dans l'acide acétique glacial.

ZUSAMMENFASSUNG

Für Titrationen in nicht-wässrigem Medium eignen sich aliphatische und aromatische Sulfosäuren unter denen besonders Methan- und Aethansulfosäure sehr gute Resultate ergeben. Von grossem Vorteil ist ihre gute Löslichkeit in Eisessig.

References p. 379

REFERENCES

[1] L. P. Hammett and N. Dietz, *J. Am. Chem. Soc.*, 52 (1930) 4795.
[2] T. L. Smith and J. H. Elliott, *Abstracts 122nd. Meeting*, American Chemical Society, Atlantic City 1952.
[3] A. Berthoud, *Helv. Chim. Acta*, 12 (1929) 859.
[4] J. S. Fritz, *Acid–Base Titrations in Nonaqueous Solvents*, The G. Frederick Smith Chemical Co., Columbus, Ohio 1952.
[5] P. C. Markunas and J. A. Riddick, *Anal. Chem.*, 23 (1951) 337.
[6] W. Seaman and E. Allen, *Anal. Chem.*, 23 (1951) 592.

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OMEGA CHROME BLUE GREEN BL AS ANALYTICAL REAGENT FOR CALCIUM AND MAGNESIUM

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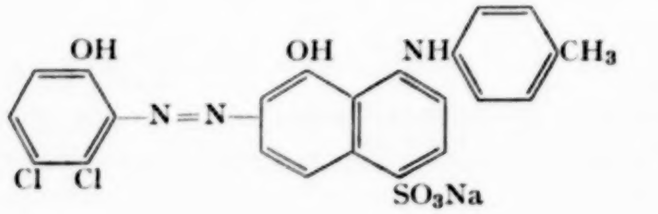
The present work describes the reaction of Omega Chrome Blue Green BL with various ions and its use as a metal indicator for the detection of equivalence points in EDTA titrations.

Properties of Omega Chrome Blue Green BL

It is a grey crystalline monoazo dye which is difficulty soluble in water to give a blue–green solution. In ethanol and acetone bright blue solutions are obtained; it is insoluble in chloroform and ether. Its Colour Index number is C.I. 17650[1], and it has the following structural formula



The effect of variation of pH on the colour of aqueous and ethanolic solutions of the dye was tested. Below pH 10.5 the colour is blue, and above 10.5 red. The maximum absorbance at pH 10 is at a wave length of 640 mμ, that of the dye–magnesium complex is at 580–600 mμ and that of the dye–calcium complex at 580–590 mμ with a flat peak.

Omega Chrome Blue Green BL metal complexes

The metal complexes of the dye were prepared by adding a few drops of an ethanolic solution of the dye to solutions of heavy metals. The pH of the solution was kept constant by addition of buffer pH 10. In testing metals which precipitate at this pH, a secondary complexing agent was added; tartrate ion was found suitable. In testing for manganese, ascorbic acid was added to prevent the formation of hydrated manganic oxide.

The results obtained showed that calcium and magnesium cause a colour change to red. Strontium and manganese show a faint colour change to violet.

The following ions failed to give a colour change: aluminium, antimony, barium, beryllium, bismuth, cobalt, cerous, copper, lead, lithium, mercury, nickel, sodium, stannous, potassium, thallium, thorium, uranium, yttrium, zirconium, zinc, acetate, borate, bromate, bromide, chloride, chlorate, citrate, cyanide, iodide, nitrate, nitrite, oxalate, phthalate, persulphate, phosphate, sulphate, sulphite, tartrate and thiocyanate.

Sensitivity of determination of calcium and magnesium

The sensitivity of the end-points of EDTA titrations of calcium and magnesium with Omega Chrome Blue Green BL as indicator was determined by placing on a spot plate one drop of buffer, one drop of 1% ethanolic dye solution and one drop (0.05 ml) of calcium or magnesium solution. Progressive dilutions of the metal standard solution were prepared and tested in the same way as long as the test gave positive results. The concentration of the diluted solution taken for the test was then calculated. By this means the identification limits were found and the corresponding dilution limits were calculated. The results (Table I) show that the indicator is suitable for the detection of end-points in the EDTA titrations of calcium and magnesium, because of reversibility and reasonably good contrast. It cannot be applied to the determination of either manganese or strontium because of the poor contrast obtained.

TABLE I

COLOUR REACTIONS OF OMEGA CHROME BLUE GREEN BL WITH METALLIC IONS

Ion	*Colour*	*Identification Limit mcg*	*Dilution limit*
Calcium	red	0.2	$1 : 2.5 \cdot 10^5$
Magnesium	red	0.12	$1 : 4.1 \cdot 10^5$
Manganese	faint red blue		
Strontium	faint red		

EXPERIMENTAL

Reagents

Indicator solution: 0.1 g of Omega Chrome Blue Green BL (Sandoz, Basle) was dissolved in 100 ml ethanol.

EDTA solution 0.01 *M:* 3.722 g of reagent grade disodium ethylenediaminetetraacetate dihydrate were dissolved in twice-distilled water and diluted to one l. This solution was standardized against standard 0.01 *M* calcium solution.

Metal salt solutions: 0.01 *M* solutions of the various metals tested were prepared from analytical grade reagents and standardized against 0.01 *M* EDTA solution using Eriochrome Black T as indicator.

Buffer solution pH 10: 13.5 g of ammonium chloride A.R. were dissolved in water, 88 ml of conc. ammonia were added and the mixture diluted to 250 ml with twice-distilled water.

PROCEDURES

Determination of calcium or magnesium

To an aliquot of the calcium or magnesium solution were added a few ml of buffer solution, 2 ml of ethanol or acetone and sufficient indicator solution to obtain a red colour. The solution was titrated with 0.01 *M* EDTA to the colour change from red to blue. The last trace of red vanishes at the end-point.

TABLE II

DETERMINATION OF CALCIUM AND MAGNESIUM WITH OMEGA CHROME BLUE GREEN BL AS INDICATOR

mg of metal		
present	*found*	*difference*
	A. calcium	
0.401	0.397	0.004
0.401	0.405	0.004
0.826	0.818	0.008
1.202	1.186	0.016
1.407	1.407	0.00
1.603	1.611	0.008
1.984	1.968	0.016
2.036	2.024	0.012
	B. magnesium	
0.243	0.253	0.010
0.486	0.491	0.005
0.730	0.39	0.009
0.973	0.985	0.012
1.216	1.224	0.008
1.459	1.464	0.005
1.702	1.700	0.002
1.945	1.955	0.010

Determination of magnesium in presence of aluminium

To the slightly acid solution of aluminium–magnesium mixture were added 1 ml of 30% triethanolamine, buffer and indicator and the magnesium was titrated as above.

TABLE III

DETERMINATION OF MAGNESIUM IN PRESENCE OF ALUMINIUM

Al added mg	*Mg added mg*	*Mg found mg*	*Error*
2.697	0.248	0.247	0.001
2.697	0.248	0.242	0.006
1.079	0.481	0.479	0.002
2.697	0.516	0.521	0.005
2.697	0.496	0.504	0.008
1.079	0.691	0.695	0.004
1.079	0.750	0.743	0.007

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RESULTS AND REMARKS

Satisfactory results were obtained by the given procedures for the determination of calcium and magnesium. The titration can be done in the cold, but better end-points are obtained at about 60°. The end-point is also improved by the addition of a few ml of acetone or ethanol.

With this indicator it is possible to titrate magnesium in presence of aluminium if aluminium is screened with triethanolamine. In this method the blue colour of the indicator remains after the end-point is reached in contrast to what usually occurs when using Erio T as indicator. It was not necessary to cool as suggested by PRIBIL[2,3], when Erio T is used as indicator. Attempts to determine aluminium by back-titration with magnesium after addition of a known excess of EDTA were unsuccessful; aluminium seems to block the indicator under these conditions.

The errors of the determinations were calculated statistically from the deviations of the results from the actual values of metal ions present and amounted to 7.2 μg for magnesium and 8.4 μg for calcium.

In contrast to Erio T, this indicator does not form red complexes with aluminium, cadmium, copper, lead, thorium, zirconium and zinc. The indicator is suitable for the direct determination of calcium, magnesium and magnesium in presence of aluminium although it does not give such sharp end-points as Erio T.

SUMMARY

The behaviour of Omega Chrome Blue Green BL towards various ions was studied. It was used as indicator in the direct EDTA titration of both calcium and magnesium and for the titration of magnesium in presence of aluminium.

RÉSUMÉ

Un indicateur est proposé pour le dosage du calcium et du magnésium par titrage au moyen de l'acide éthylènediaminotétracétique et pour le titrage du magnésium en présence d'aluminium.

ZUSAMMENFASSUNG

Als neuer Indikator für die komplexometrische Titration von Calzium und Magnesium sowie von Magnesium in Gegenwart von Aluminium wird Omega Chrom Blaugrün BL vorgeschlagen.

REFERENCES

[1] The Society of Dyers and Colourists, *Colour Index*, Vol. 1, 1956, p. 1544.
[2] R. PRIBIL, *Chem. listy*, 48 (1954) 382.
[3] R. PRIBIL, *Collection Czechoslov. Chem. Communs*, 19 (1954) 465.

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THE INTERSTITIAL VOLUME OF ION-EXCHANGE COLUMNS

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The volume outside of the resin particles in an ion-exchange column is called the interstitial, void, or free volume and is often denoted by V. In the plate theory of ion-exchange elution chromatography[1] and of the closely related salting-out[2] and solubilization[3] types of chromatography, the interstitial volume is an important parameter. The distribution ratio, C, (the quantity of any particular solute in the resin phase of any plate divided by the quantity in the interstitial solution of the same plate) is readily calculated from an experimental elution graph by the equation

$$C = (U^*/V) - 1 \qquad (1)$$

where U^* is the volume of eluate collected from the addition of the sample to the peak of the elution graph. Thus any error in the determination of V introduces an error in the value of C.

The values of V/V_b (the ratio of the interstitial volume to the bed volume) reported in the literature range from 0.25 to 0.819. The former figure was calculated[4] on the erroneous assumption that the resin consisted of spherical beads of uniform size packed as closely as possible. To find the latter value, the volume of resin in the bed was assumed[5] to be equal to the weight of dried resin divided by its density. Thus this value includes the interstitial and imbibed water. KRAUS AND MOORE[6] found a value of 0.40 for Dowex-1 (crosslinkage not stated, probably about 8%) by measuring U^* for an unabsorbed species ($C = 0$) and using equation (1).

HARRINGTON[7] found values of V/V_b ranging from 0.385 to 0.396 for glass beads. He determined the interstitial water both by addition of water to the dry beads and by measurement of the water removed by centrifugation. Values within this narrow range were obtained both with uniform beads of 200-mesh and of 250-mesh and with a mixture of beads of 100-, 150-, and 200-mesh. If it can be assumed that that spherical beads of resin of approximately the same size as the glass beads are packed in a column similarly to the glass beads, HARRINGTON's values are applicable to resin columns. He also equilibrated beads of 20–50 mesh, sodium-form Dowex 50-X8 with saturated water vapor then treated them analogously to the glass beads, finding a mean of 0.390 for V/V_b. He treated dried beads of 20–50 mesh, hydrogen-form Dowex 50-X8 analogously, using octane instead of water, and found 0.387.

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Changes to 50–100 mesh or to the sodium form caused only minor changes (maximum of 0.015) from this value.

The method previously used in this laboratory[8] consists in equilibrating a column of resin with standard hydrochloric acid, draining the column to the upper level of the resin, rinsing the interstitial acid from the column with water and determining the amount of this acid by titration with sodium hydroxide. This quantity of acid, expressed in mequivs, divided by the normality of the standard acid, was taken as the interstitial volume. Corrections were applied for the quantity of acid in the filter disk and on the inside walls of the chromatographic tube below the filter disk. This method, or minor modifications of it, has yielded values of V/V_b ranging from 0.34[9] to 0.59. The latter value was found for a resin that consisted of irregularly shaped particles[10].

An error is inherent in the foregoing method. According to the DONNAN principle, some hydrochloric acid will penetrate the resin beads and be removed by the rinse water. This leads to high results.

The work reported in this paper was undertaken (1) to ascertain the magnitude of the error due to the DONNAN penetration, (2) to develop a reliable method for the determination of interstitial volume and (3) to investigate the effects of size, degree of crosslinkage, and chemical nature of the resin on the interstitial volume. Since very large ions are unable to diffuse into the resin, polyelectrolytes were substituted for hydrochloric acid in some of the experiments in order to eliminate the DONNAN penetration. In other experiments, hydrochloric acid was used as the interstitial solution; and a correction for the penetration was applied mathematically.

CORRECTION FOR THE PENETRATION OF HYDROCHLORIC ACID INTO THE RESINS

The uncorrected interstitial volume is

$$V_u = L/N \qquad (2)$$

where N is the normality of the interstitial hydrochloric acid and L is the number of mequivs. of acid rinsed from the column. If λ denotes the quantity (in mequivs.) of hydrochloric acid that penetrates the resin per gram of dry resin and if W denotes the dry weight of resin in the column, the corrected interstitial volume is

$$V = V_u - \frac{\lambda W}{N} \qquad (3)$$

Cation-exchange resins

For sulfonated crosslinked polystyrenes in the hydrogen form it has been shown[11] that

$$V_r = (1.003\theta + 0.628)W \qquad (4)$$

where V_r is the volume of swollen resin in the column and θ is the weight (in grams) of water imbibed per gram of dry resin. An approximate form of this equation

$$V_r = (\theta + 0.63)W \qquad (5)$$

is satisfactory for our purpose. The value 0.63 may be regarded as the specific matrix volume of the swollen resin.

Also

$$V_r = V_b - V \quad \ldots\ldots\ldots\ldots \quad (6)$$

From equations (3), (5), and (6)

$$\frac{V}{V_b} = \frac{\dfrac{V_u}{V_b} - B}{1 - B} \quad \ldots\ldots\ldots\ldots \quad (7)$$

where

$$B = \frac{\lambda}{(\theta + 0.63)N} \quad \ldots\ldots\ldots\ldots \quad (8)$$

If the values of λ and θ are known for any given resin and concentration of hydrochloric acid, the corresponding value of B can be calculated by equation (8). Then the corrected value of V/V_b can be calculated for that resin by equation (7). PEPPER, REICHENBERG AND HALE[11] have determined λ and θ for several sulfonated polystyrene resins of various crosslinkages in several different concentrations of hydrochloric acid. Their data are summarized in Table I. Since the concentrations of hydrochloric acid and the degrees of crosslinking of the resins in our work differed from those of PEPPER *et al.*, it was neccessary to perform a double interpolation on the data of Table I in order to find the appropriate B values. These interpolated values are given in Table II.

TABLE I

VALUES OF B FOR SULFONATED POLYSTYRENE

Normality of HCl	*Degree of crosslinking*			
	2	*5*	*10*	*15*
0.00	0.000	0.000	0.000	0.000
0.11	0.096	0.085	0.000	0.000
0.52	0.218	0.055	0.013	0.016
1.05	0.322	0.090	0.026	0.016
2.30	0.411	0.163	0.055	0.014

TABLE II

INTERPOLATED VALUES OF B FOR SULFONATED POLYSTYRENE

Normality of HCl	*Degree of crosslinking*			
	2	*4*	*8*	*16*
0.01	0.020	0.005	0.001	0.000
0.1	0.090	0.035	0.005	0.000

Anion-exchange resins

Adequate data for the values of λ and θ for strong-base anion-exchange resins of the type of Dowex 1 have not been recorded in the literature. For this reason, the penetration of water and of hydrochloric acid into several samples of Dowex 1 of various crosslinkages from water and from 0.01 *N* and 0.1 *N* aqueous hydrochloric acid was determined in the course of this investigation.

EXPERIMENTAL

Materials

Several samples of Dowex 50 and of Dowex 1 of various degrees of crosslinking and various mesh sizes were used.

A sample of Graham salt (sodium polyphosphate) was prepared by fusion of primary sodium phosphate at about 940° for 12 h and rapid cooling of the melt between steel plates. A solution of this polymer was prepared to be 0.01 *M* with respect to the monomeric unit; it was standardized by a spectrophotometric method[12].

Professor U. P. STRAUSS[13] kindly donated samples of poly-4-vinyl-N-ethylpyridinium bromide, $(CH_2\text{-}CHC_5H_4NEtBr)_n$, and a similar compound in which 15% of the alkyl groups were dodecyl, the remaining 85% being ethyl. The latter compound is hereinafter designated as "polysoap." The number-average degree of polymerization of the polyvinylethylpyridinium bromide was 265. That of the polysoap was of the order of 2000. Solutions of these compounds, 0.01 *M* with respect to the monomeric unit, were prepared; they were standardized by the Volhard method.

Measurement of the absorption of water and of hydrochloric acid by Dowex 1

Samples of Dowex 1 of various crosslinkages were equilibrated with water or standard hydrochloric acid and transferred to weighed centrifuge tubes provided with a filter disk[11]. After centrifugation to remove the interstitial liquid, the tubes and moist resin were weighed. The resins were then washed with water to remove the hydrochloric acid that had penetrated into the resin, and the washings were titrated with sodium hydroxide. The tubes and resins were then dried at 110° in a vacuum and reweighed. Corrections of 0.033 ml per ml of resin bed[14] were applied for the interstitial liquid that was not removed by the centrifugation. A correction was also applied for the amount of water and hydrochloric acid remaining in the filter disk. These measurements furnished the data needed to calculate θ and λ. Pycnometric measurements were made in water to determine the specific matrix volumes of these resins.

Determination of interstitial volume

The interstitial volumes of hydrogen-form Dowex 50 and of chloride-form Dowex 1 were determined with hydrochloric acid as previously described[8].

Sodium polyphosphate was used with sodium-form Dowex 50 as follows. The resin was slurried with water and poured into a chromatographic tube of known internal diameter. After the resin settled (about 5 min), one l of water was passed through the column. The water in the tube was drained to the level of the resin. Then about three bed volumes of the polyphosphate solution were passed through the column to displace the interstitial water. The liquid in the tube was again drained to the level of the resin, and the height of the resin column was measured. The procedure was continued as with hydrochloric acid except that a spectrophotometric method[12] was used to determine the amount of polyphosphate in the eluate.

Solutions of the polysoap and of the poly-4-vinyl-N-alkylpyridinium bromide were applied similarly to determine the interstitial volumes of Dowex 1 in the bromide form and Dowex 50 in the hydrogen, lithium, and barium forms. The bromide washed from the interstices was determined by the Volhard method.

RESULTS AND DISCUSSION

Absorption of water and hydrochloric acid by Dowex 1

The specific matrix volumes of the anion-exchange resins were calculated from the pycnometric measurements as $1 - (W_3 - W_2)/W_1$ where W_3 is the weight of the pycnometer containing W_1 grams of dry resin and enough water to fill it, and W_2 is the weight of the pycnometer full of water. The values for Dowex 1-X2, X4, X8, and X10 were 0.856, 0.847, 0.845, and 0.856, respectively. The average was rounded to 0.85. Thus for these resins, instead of equation (8), the appropriate equation is

$$B = \frac{\lambda}{(\theta + 0.85)N} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Since Dowex 1 is less dense than Dowex 50, the larger value of the specific matrix volume is to be expected.

The absorption of hydrochloric acid, λ, and of water, θ, also the calculated values of B, are listed in Table III.

As is to be expected, the absorption of water shows a regular decrease with increasing crosslinkage. This is not the case with the absorption of hydrochloric acid, λ, which seems to vary erratically. This suggests strongly that some phenomenon in addition to the DONNAN effect is causing hydrochloric acid to enter the resin beads during the equilibration and to leave them during the washing process. The presence in the resin of a relatively small number (varying erratically form batch to batch) of tertiary and secondary nitrogen atoms would account for the results in Table III. Evidence for the existence of such weakly basic groups in Dowex 1 has been observed by other investigators[14, 15]. When the resin is equilibrated with hydrochloric acid, these weakly basic groups are neutralized; but they release the acid by hydrolysis when the resin is washed with water. Thus only a part of the absorption of hydrochloric acid is due to the DONNAN effect.

Because of the variability of Dowex 1 from batch to batch, the λ-values of Table III are not applicable to other samples of Dowex 1. Nevertheless, the data of Table III are valid for calculating the corrected interstitial volumes by equations (9) and (8) provided the same batches of resins are used for the determination of interstitial volume as were used to obtain the data of Table III. This precaution was observed.

TABLE III

ABSORPTION OF WATER AND HYDROCHLORIC ACID BY ANION-EXCHANGE RESINS

Resin	*0.01 N hydrochloric acid*			*0.1 N hydrochloric acid*		
	λ	θ	*B*	λ	θ	*B*
Dowex 1-X2	0.0135	3.45	0.313	0.083	3.41	0.194
Dowex 1-X4	0.0018	1.55	0.075	0.016	1.47	0.069
Dowex 1-X8	0.0025	0.54	0.167	0.0158	0.64	0.105
Dowex 1-X10	0.0069	0.59	0.476	0.0176	0.59	0.121

TABLE IV

RELATIVE INTERSTITIAL VOLUMES OF RESINS, 200–400 MESH

Resin	*Hydrochloric acid*				*Poly-phosphate 0.01 M*	*Polysoap 0.01 M*	*Polyvinyl-ethylpyridinium bromide 0.01 M*	*Mean*	*Standard deviation*
	0.01 M		*0.1 M*						
	*Uncorrd.**	*Corrd.*	*Uncorrd.**	*Corrd.*					
Dowex 50-X2	0.317	0.303	0.376	0.314	0.289	0.308	0.330*	0.304	0.010
Dowex 50-X4	0.350	0.346	0.358	0.335	0.307	0.321	0.362*	0.327	0.017
Dowex 50-X8	0.385	0.384	0.391	0.388	0.365	0.378	0.439*	0.379	0.010
Dowex 50-X16	0.383	0.383	0.385	0.385	0.404	0.408	0.404*	0.395	0.016
Dowex 1-X2	0.571	0.375	0.487	0.363		0.330	0.335	0.351	0.022
Dowex 1-X4	0.406	0.358	0.412	0.368		0.338	0.338	0.350	0.012
Dowex 1-X8	0.479	0.374	0.442	0.376		0.409	0.400	0.390	0.015
Dowex 1-X10	0.672	0.375	0.452	0.377		0.421	0.412	0.396	0.024

* Excluded from mean.

Comparison of the various methods

Table IV shows the relative interstitial volumes of spherical beads, 200–400 mesh, of Dowex 50 and Dowex 1 of various degrees of crosslinking as determined by the several methods. Most of the entries are the means of three determinations, whose standard deviations never exceeded 0.016.

Sodium polyphosphate (Graham salt) contains about 4% of sodium trimetaphosphate and a smaller percentage of sodium tetrametaphosphate[16]. These compounds, because of their small concentration, would not enter Dowex 50 by the DONNAN effect appreciably; therefore sodium polyphosphate gave satisfactory results for V/V_b of this resin. On the other hand, the metaphosphate anions would enter the beads of Dowex 1 and exchange with the chloride; therefore the interstitial volume of this resin could not be determined with sodium polyphosphate.

The table indicates that satisfactory agreement for the relative interstitial volume of Dowex 50 is obtained with polyphosphate, polysoap, or hydrochloric acid of either concentration (provided that the correction for the DONNAN effect is applied).

The results for V/V_b of Dowex 50 obtained with the polyvinylethylpyridinium bromide are abnormally high. The following hypothesis is offered to explain this discrepancy. Because of the repulsion of the positive charges on quaternary nitrogen atoms, the molecules of this polymer are almost linear in shape. The exchange of any one quaternary ammonium ion with a hydrogen ion of a sulfonic acid on (or slightly below) the surface of a resin bead will serve to hold the entire polymeric molecule in the vicinity of the resin bead. Thus, after equilibration with the solution of this polycation, each resin bead is probably covered by a swarm of polymer molecules, each of which is held to the resin by one (or very few) electrovalent bond. When the interstitial solution is removed by washing, most of these surface-held polymers are washed away, and the remaining polymers are held by several electrovalents bonds. Thus the quantity of this polymer washed from the resin is greater than the quantity that was in the interstitial solution.

The presence of dodecyl groups in the polysoap, by virtue of van der Waals forces, causes the molecules of this polymer to become approximately spherical in shape[13]. Therefore the polysoap does not behave toward the resin like the polyvinylethylpyridinium bromide.

The error caused by the penetration of 0.01 N hydrochloric acid in this resin is less than the experimental error (±0.02) for all the degrees of crosslinking studied. However, with 0.1 N hydrochloric acid, this error is significant with 4% or less of divinylbenzene.

The agreement among the various methods is somewhat less satisfactory for Dowex 1 than for Dowex 50. The correction for the hydrochloric acid taken up by the anion-exchange resin and released during washing is significant for both concentrations of acid and for all the degrees of crosslinking studied. As mentioned above, this sorption and release of hydrochloric acid by Dowex 1 are due not only to the DONNAN effect but also to the presence of a small number of weakly basic groups in the resin.

Both cation- and anion-exchange resins have smaller interstitial volumes when the crosslinkage is small. This is probably due to the greater deformability of the resins of low crosslinkage.

Dowex 50 seems to have a slightly smaller interstitial volume than Dowex 1 of the same crosslinkage, especially if the degree of crosslinking is small. This may be due to the greater density of Dowex 50, which would result in better settling and closer packing of the column.

The relative interstitial volumes (V/V_b) of Dowex 50-X8, 200–400 mesh, in the lithium and barium forms were determined with the polysoap and found to be 0.400 and 0.402, respectively. Since these results do not differ greatly from the value for the hydrogen form (Table IV), it is concluded that the form of the resin influences the relative interstitial volume to a small extent only.

Several samples of Dowex 50-X8 of various mesh sizes, all in the hydrogen form, were subjected to determinations of V/V_b with 0.01 N hydrochloric acid. These results indicate that the particle size has only an insignificant effect on the interstitial volume, provided, of course, that the range of sizes is not so great that the smallest particles pack in the interstices of the large particles.

When any ion-exchange resin, especially one of low crosslinkage, is exposed to a concentrated aqueous solution, the particles become smaller and more rigid than when they are in contact with water or a dilute solution. For this reason, it is doubtful if the results of Table IV, obtained with dilute solutions, are valid for concentrated solutions. To investigate this point, Dowex 50-X2, 200–400 mesh, was converted to the sodium form, equilibrated with 1 M or 5 M sodium nitrate and subjected to determinations of V/V_b by the use of polyphosphate. Since sodium polyphosphate has very limited solubility in these concentrations of sodium nitrate, solutions of the polyphosphate as low as 0.0001 M (with respect to the monomeric unit) were prepared in the water or aqueous sodium nitrate as solvent. The results are given in Table V.

Two conclusions may be drawn from these results. (1) Within the range of concentrations of polyphosphate used for the determination of the interstitial volume, the concentration of this compound has no effect on the result. (2) The interstitial volume increases markedly as the concentration of ambient sodium nitrate is increased from 0 to 5 M. It is noteworthy that the relative interstitial volume of Dowex 50-X2 in 5 M sodium nitrate agrees within the experimental error of 0.02 with the values of Dowex 50-X8 or -X16 in water. This probably means that the X2 resin in 5 M sodium nitrate has approximately the same degree of rigidity as the X8 or X16 resins in water.

TABLE V

RELATIVE INTERSTITIAL VOLUMES OF DOWEX 50-X2 IN SOLUTIONS OF SODIUM NITRATE

Interstitial liquid	*Concentration of polyphosphate*			
	0.01 M	*0.001 M*	*0.0002 M*	*0.0001 M*
Water	0.289	0.294		0.284
1 M $NaNO_3$		0.327		
5 M $NaNO_3$			0.385	0.381

Finally, it should be noted that irregularly shaped resins have much greater relative interstitial volumes than do spherical resins[10].

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SUMMARY

The relative interstitial volumes of ion-exchange columns were measured by equilibrating the columns with a standard solution, rinsing out the interstitial solution and determining the amount of solute in the rinsings. Solutions of three polyelectrolytes and of hydrochloric acid were used for this purpose. When hydrochloric acid was used, corrections were generally necessary because of the penetration of the acid into the resin. Satisfactory agreement was obtained among the various methods. Within the experimental error, the relative interstitial volume is independent of the exchangeable ion of the resin and of the mesh size. The interstitial volume decreases with decreasing crosslinkage.

RÉSUMÉ

Les volumes intersticiels relatifs de colonnes d'échangeurs d'ions ont pu être mesurés. Pour cela, on a équilibré les colonnes avec une solution étalon, rincé la solution intersticielle et déterminé la teneur en solute des eaux de rinçage. Le volume intersticiel relatif est indépendant de l'ion échangeable de la résine et de la grosseur de ses grains.

ZUSAMMENFASSUNG

Zur Messung des relativen interstitiellen Volumens von Ionenaustauscher-Kolonnen wurden Standardlösungen mit den Kolonnen ins Gleichgewicht gebracht und nach Auswaschen der Kolonnen der Gehalt an gelöster Substanz in dem Waschwasser bestimmt. Das relative interstitielle Volumen erwies sich als unabhängig vom austauschbaren Ion und der Korngrösse des Harzes.

REFERENCES

[1] W. RIEMAN AND R. SARGENT, "*Ion Exchange*," in W G. Berl, *Physical Methods in Chemica Analysis*, vol. IV, Academic Press, New York, in press.
[2] R. SARGENT AND W. RIEMAN, *J. Phys. Chem.*, 61 (1957) 354.
[3] J. SHERMA AND W. RIEMAN, *Anal. Chim. Acta*, 18 (1958) 214.
[4] H. P. GREGOR AND M. TETENBAUM, *J. Phys. Chem.*, 58 (1954) 1156.
[5] S. W. MAYER AND E. R. TOMPKINS, *J. Am. Chem. Soc.*, 69 (1947) 2866.
[6] K. A. KRAUS AND G. E. MOORE, *J. Am. Chem. Soc.*, 75 (1953) 1460.
[7] D. HARRINGTON, private communication.
[8] R. SARGENT AND W. RIEMAN, *Anal. Chim. Acta*, 18 (1958) 197.
[9] R. SARGENT AND W. RIEMAN, *Anal. Chim. Acta*, 17 (1957) 408.
[10] A. BREYER AND W. RIEMAN, *Anal. Chim. Acta*, 18 (1958) 204.
[11] K. W. PEPPER, D. REICHENBERG AND D. K. HALE, *J. Chem. Soc.*, (1952) 3129.
[12] J. BEUKENKAMP, W. RIEMAN AND S. LINDENBAUM, *Anal. Chem.*, 26 (1954) 505.
[13] U. P. STRAUSS AND N. L. GERSHFELD, *J. Phys. Chem.*, 58 (1954) 747.
[14] K. A. KRAUS AND G. E. MOORE, *J. Am. Chem. Soc.*, 75 (1953) 1457.
[15] H. P. GREGOR, J. BELLE AND R. A. MARCUS, *J. Am. Chem. Soc.*, 76 (1954) 1984.
[16] T. V. PETERS, JR., AND W. RIEMAN, *Anal. Chim. Acta*, 14 (1956) 131.

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SPECTRAL DETECTION OF TERMINAL RING QUINONES

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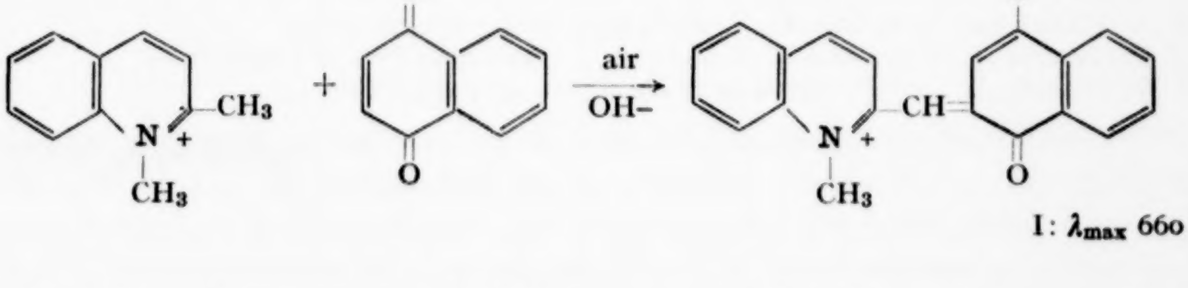
INTRODUCTION

Specific colorimetric methods for the analysis of all types of quinones are in critical need. Terminal ring quinones, such as benzoquinone and α-naphthoquinone, have been detected with ethyl malonate in alkaline solution[1]. KESTING has reported that color tests are given by benzoquinone, α-napthoquinone and β-naphthoquinone in alkaline alcoholic solution on reaction with malononitrile, ethyl benzoylacetate, acetylacetone, or benzoylacetone[2-4]. CRAVEN[5] has obtained brilliant, although unstable, color reactions for benzoquinone, *o*-toluquinone, chloranil, thymoquinone, and α-naphthoquinone with ethyl cyanoacetate in alcoholic ammonia. β-Naphthoquinone did not react. In dilute alkali, nitromethane is stated to give a blue color with α-naphthoquinone and a violet color with β-naphthoquinone[6]. In our laboratory, many of these reagents were tried in alkaline 2-methoxyethanol solution. In many cases unstable colors and insensitive reactions were obtained. For this reason a group of new reagents for the colorimetric analysis of quinones is introduced in this paper.

Quinones giving a positive test contain the grouping $O{=}\overset{|}{C}{-}\overset{|}{C}{=}\overset{|}{C}{-}X$, where X is hydrogen or halogen. The reagents are azonium heterocyclic derivatives containing an activated methyl group *ortho* or *para* to the azonium nitrogen. The mechanism involves addition of the methyl group to the activated double bond of the quinone followed by air oxidation to a blue or green dye, *e.g.* with *N*-methylquinaldinium iodide and α-naphthoquinone the following reaction takes place:



I: λ_{max} 660 mμ

The dye, I, has been prepared by KIPRIANOV[7] and absorbs at 670 mμ in alcohol.

EXPERIMENTAL

Reagents

Lepidine, quinaldine, 2-methylbenzoxazole, 2-methylbenzothiazole, 1-ethyl-quinaldinium iodide, and 1-ethyl-2,6-dimethylquinolinium iodide were obtained from Distillation Products; 6-ethoxyquinaldine was obtained from the Aldrich Chemical Co.

The azonium methosulfates were prepared by slightly modified procedures of the following preparation of 1-methyl-quinaldinium methosulfate: 28 g of quinaldine and 25 g of methyl sulfate were mixed thoroughly in an ice bath. The mixture was allowed to stand at room temperature until an exothermic reaction had taken place and the mixture had solidified. The product was crystallized from *n*-propyl alcohol. The 6-ethoxy derivative was prepared in a small volume of boiling acetone; the lepidine derivative was prepared at room temperature. Details of these preparations can be found in the literature[8].

Benz [e] acephenanthrylene-9,12-dione, m.p. 248–249°, was prepared by literature procedure[9].

Equipment

A Cary Model 11 Recording spectrophotometer was used for wave-length measurements. For time studies an American Optical Company Rapid Scan Spectrophotometer was used.

Test procedure

To an accurately measured 5–50 ml of the 2-methoxyethanol test solution was added 1 ml of a 2% 2-methoxyethanol solution of the quinolinium reagent. The mixture was shaken, and after 8–9 min it was diluted to approximately 50 ml with 2-methoxyethanol. Ten min after the addition of reagent, 2 ml of 10% aqueous tetraethylammonium hydroxide was added, followed by dilution of the mixture to 100 ml with 2-methoxyethanol. Within ten min the absorption spectrum was determined from 500–800 mμ. The data on the more intense and much more stable long wave-length band are reported in Table I. One-tenth the volumes can also be used in the procedure.

TABLE I

SPECTRAL DETECTION OF TERMINAL RING QUINONES

Compound	λ_{max} *(sens.)* [a]				
	1,2-Dime [b]	*1-Et-2-me* [c]	*1-Et-2,6-dime* [c]	*1,2-Dime-6-etO* [b]	*1,4-Dime* [b]
Benzoquinone	650 (0.007)	655 (0.010)	670 (0.006)	685 (0.006)	700 (0.008)
2,5-Dichlorobenzoquinone	655 (0.012)	685 (0.025)	660 (0.025)	670 (0.014)	715 (0.014)
Chloranil	655 (0.013)	660 (0.020)	660 (0.090)	670 (0.008)	715 (0.023)
1,2-Naphthoquinone	670 (0.060)	670 (0.060)	660 (0.060)	635 (0.060)	720 (0.057)
Sodium 1,2-naphthoquinone -4-sulfonate	660 (0.045)	670 (0.30)	655 (0.045)	640 (0.040)	685 (0.044)
1,4-Naphthoquinone	660 (0.023)	660 (0.023)	675 (0.019)	685 (0.013)	700 (0.020)
2-Methyl-1,4-naphthoquinone	635 (0.043)	675 (0.070)	650 (0.041)	665 (0.027)	670 (0.027)
2,3-Dichloronaphthoquinone	675 (0.15)	675 (0.027)	690 (0.014)	700 (0.012)	720 (0.019)
Benz[e] acephenanthrylene -9,12-dione	715 (0.025)	670 (0.022)	735 (0.020)	750 (0.025)	775 (0.10)

[a] In μmoles per 3 ml giving an optical density of 0.1 in a cell of 1-cm path length.
[b] Quinolinium methosulfate.
[c] Quinolinium iodide.

DISCUSSION

In a previous paper a novel thermochromic test for polynuclear inner-ring *p*-quinones was described[10]. With this test the presence of large polynuclear *p*-quinonic type compounds was demonstrated in air particulates. In the present tests inner-ring *o*- and *p*-quinones, such as phenanthraquinone, 5,6-chrysenequinone anthraquinone, and naphthacenequinone gave negative results. Other types of aromatic carbonyl compounds, such as anthanthrone, benzanthrone, fluorenone, benzophenone, acetophenone, benzalacetone, salicaldehyde, 2-hydroxy-1-naphthaldehyde, and *p*-dimethylaminobenzaldehyde also gave negative results. As far as could be determined the tests described in this paper are specific for terminal-ring quinones.

Many activated methylene compounds were found to give color reactions with terminal ring quinones in alkaline dimethylformamide or 2-methoxyethanol solution, *e.g.* nitromethane, malonitrile, diketene, 3-thenoyl-1,1,1-trifluoroacetone, benzoylacetonitrile, 3-ethylrhodanine, 3-methyl-1-phenyl-5-pyrazolone, ethoxymethylenemalononitrile, and diethyl ethoxymethylenemalonate.

The nonketonic methylene reagents (*e.g.* malononitrile, nitromethane, etc.) gave unstable colors under the conditions of the procedure, while the ketonic methylene reagents apparently reacted with themselves slowly in alkaline solution to give colored dyes. This self-condensation is indicated by a study of the stability of the color obtained in the reaction of 3-ethylrhodanine with chloranil. Visually the color of the solution changed drastically with time while spectrally the 650 mμ band changed but slightly over a period of one-half hour, Fig. 1. The color change from green to dirty brown is due to the reaction of 3-ethylrhodanine, probably with itself, to give a dye absorbing at 530 mμ. This byproduct interferes with the color test but not with the spectral test.

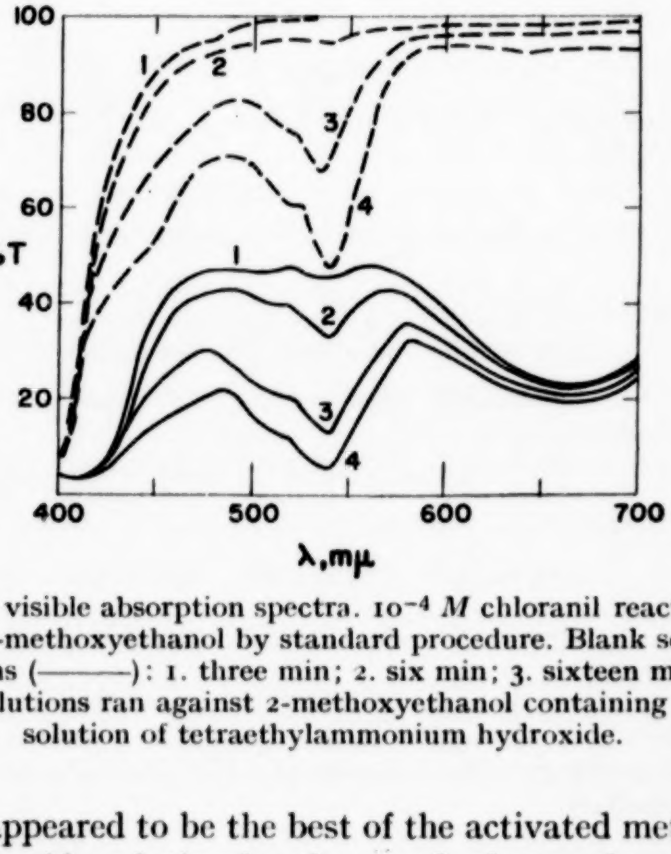


Fig. 1. Effect of time on visible absorption spectra. 10^{-4} *M* chloranil reacted with a 2% solution of 3-ethylrhodanine in 2-methoxyethanol by standard procedure. Blank solutions (minus chloranil) (– – –); Test solutions (———): 1. three min; 2. six min; 3. sixteen min; 4. thirty min, after addition of alkali. All solutions ran against 2-methoxyethanol containing 2% of a 10% aqueous solution of tetraethylammonium hydroxide.

3-Ethylrhodanine appeared to be the best of the activated methylene compounds, *e.g.*, in dimethylformamide solution by the standard procedure – with *p*-benzoquinone, λ_{max} 635 mμ, sens. 0.007; chloranil, λ_{max} 650 mμ, sens. 0.04; 2,3-dichlorobenzoquinone, λ_{max} 660 mμ, sens. 0.01; 1,4-naphthoquinone, λ_{max} 715 mμ, sens. 0.025; 2-methyl-1,4-naphthoquinone, λ_{max} 720 mμ, sens. 0.05; 2,3-dichloro-1,4-naphthoquinone, λ_{max} 705 mμ, sens. 0.05, and benz[e]acephenanthrylene-9,12-dione, $\lambda_{max} >$ 800 mμ. 1,2-Naphthoquinone and its 4-sodium sulfonate derivative gave green colors which faded rapidly. 2-Hydroxy-1,4-naphthoquinone gave negative results with all the reagents.

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Of all the compounds tried as reagents, the quinaldinium derivatives gave the most sensitive and stable colors (green in all instances) (Table I). The wave-length maxima for the dyes formed in the test ranged from 635–775 mμ. In most cases the benzoquinone derivatives gave the most sensitive reaction while the two 1,2-naphthoquinone derivatives gave the least sensitive reaction. If the quinones are analyzed within 10 min after they are reacted with a quinolinium derivative, there is very little change in the color or intensity of the long wave-length band. Over a period of 1–1/2 h, new bands arise near 560 mμ and gradually increase in intensity, eventually interfering with the analysis in the long wave-length region (Fig. 2).

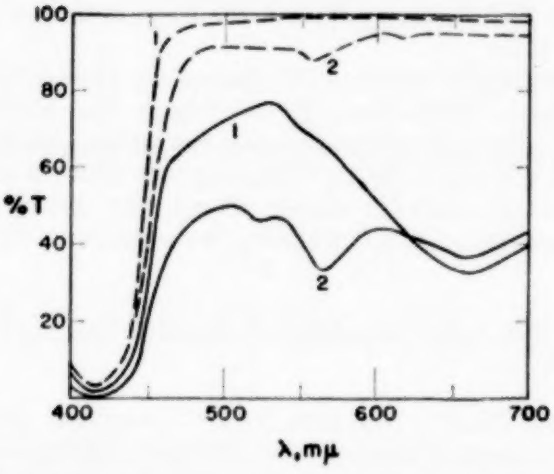

Fig. 2. Effect of time on visible absorption spectra. $2 \cdot 10^{-5}$ *M* chloranil reacted with a 2% solution of 1-ethyl-2,6-dimethylquinolinium iodide in 2-methoxyethanol by standard procedure. Blank solution (minus chloranil) (- - -); Test solutions (———); 1. three min; 2. eighty min, after addition of alkali. All solutions ran against 2-methoxyethanol containing 2% of a 10% aqueous solution of tetraethylammonium hydroxide.

SUMMARY

Terminal ring quinones can be detected specifically by a simple spectroscopic method involving reaction of the quinone with quinaldinium or lepidinium salts in alkaline solution. Other types of quinones and carbonyl derivatives have given negative results. 3-Ethylrhodanine can also be used as a reagent, especially for terminal ring *p*-quinones. All of these colorimetric procedures are amenable to quantitation.

RÉSUMÉ

Un groupe de nouveaux réactifs est proposé pour l'analyse colorimétrique de quinones.

ZUSAMMENFASSUNG

Chinone lassen sich colorimetrisch mit Hilfe von Chinaldin-oder Lepidin-salzen in alkalischem Medium nachweisen.

REFERENCES

[1] C. Liebermann, *Ber.*, 10 (1877) 1614.
[2] W. Kesting, *Z. angew. Chem.*, 41 (1928) 358, 745.
[3] W. Kesting, *Ber.*, 62B (1929) 1422.
[4] W. Kesting, *J. prakt. Chem.*, 138 (1933) 215.
[5] R. Craven, *J. Chem. Soc.*, (1931) 1605.
[6] W. Brackman and E. Havinga, *Rec. trav. chim.*, 74 (1955) 1021.
[7] A. I. Kiprianov and A. V. Stetsenko, *Zhur. Obshcheĭ Khim.*, 23 (1953) 1912.
[8] J. Williams and J. Nys, *Bull. soc. chim. Belges*, 66 (1957) 502.
[9] N. Campbell and H. Wong, *J. Chem. Soc.*, (1949) 1513.
[10] E. Sawicki, T. W. Stanley and T. R. Hauser, *Anal. Chem.*, 30 (1958) 2005.

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BOOK REVIEWS

GMELINS *Handbuch der anorganischen Chemie.* 8. Auflage, Verlag Chemie, G.m.b.H., Weinheim, 1958/9.
Fluor (Ergänzungsband), System-Nummer 5, 258 Seiten, kartoniert DM 145,—, Ganzleinen DM 150.—.

Dieser Ergänzungsband, der Prof. Dr. OTTO HAHN gewidmet ist, umfasst die Forschungsergebnisse der Jahre 1926 bis 1949. In diese Periode fällt die zunehmende Bedeutung der Fluorchemie, die zum Teil auf der Erkenntnis der Bedeutung des Fluors in der Zahnheilkunde beruht, zum grossen Teil aber auf die Entwicklung fluorierter Polymere mit technisch sehr interessanten Eigenschaften zurückzuführen ist.

Die Einteilung folgt dem üblichen Schema: Vorkommen, Darstellung, physikalisches und chemisches Verhalten, analytische Methoden. Dann folgen die Verbindungen mit Wasserstoff, Sauerstoff und Stickstoff mit Angabe der Darstellungsmethoden. Im Kapitel über die Herstellungsmethoden wird besonders auf die Gefahren im Umgang mit Fluor hingewiesen.

Als begrüssenwerte Neuerung enthält dieser Band ein zusätzliches Inhaltsverzeichnis in englischer Sprache sowie marginale Inhaltsangabe der einzelnen Kapitel ebenfalls in englischer Sprache.

Silicium, Teil C: *Organische Siliciumverbindungen.* System-Nummer 15, 501 Seiten, kartoniert DM 276.—, ganzleinen DM 281.—.

Mit dem jetzt erschienenen Band ,,Silicium Teil C" beginnt die neue System Nr. 15. Der vorliegende Teil C behandelt ausschliesslich die Organo-Siliciumverbindungen, die durch die Entwicklung der Silikone eine überragende Bedeutung erlangt haben. Der grösste Teil dieses Bandes behandelt die Methoden der Darstellung dieser Verbindungen und beschreibt deren Eigenschaften, wobei eine Einteilung in Tetraalkyl-, Alkylhydrogen-, Halogen-, Thio-, Amino- und Alkoxysilane, Silanole, Siloxane und Kieselsäureester erfolgte. Insgesamt werden mehr als 3000 Verbindungen, teils einzeln, teils gruppenweise zusammengefasst, aufgeführt. Etwa 100 Seiten sind einer Behandlung der Chemie der Silikone gewidmet, wobei auch spezielle Herstellungsfragen berücksichtigt wurden. Anschliessend werden die Anwendungsmöglichkeiten der Silikone. (als Oele, Pasten, Fette und Harze) einschliesslich des Silikonkautschuks und anderer Spezialprodukte besprochen.

Der Band enthält ein Inhaltsverzeichnis in deutscher und englischer Sprache und ausserdem auf den Inhalt der einzelnen Kapitel durch Randbeschriftung (englisch).

K. EDER (Genf)

English for the Scientist par Cl. DUVAL - Edition CNRS, 5ème Ed., Paris 1958, 99 pages, fr. 500.—.

La 5ème édition, revue et corrigée, de ce manuel est sortie de presse; c'est dire combien ce livre de vocabulaire scientifique et technique, et de syntaxe est apprécié de tous ceux qui désirent pouvoir se servir d'une langue dans laquelle une grande partie de la science d'aujourd'hui est écrite.

L'oeuvre est conçue de telle façon que chimiste, physicien et mathématicien, aussi bien que biologiste et médecin y trouveront à leur convenance les termes et constructions de phrase qu'ils peuvent rencontrer en feuilletant articles ou livres anglais. En outre, il permet à tous ceux qui le désirent, de s'approprier une connaissance suffisante d'anglais technique, qui leur permettra d'écrire, de suivre une discussion, de s'exprimer dans cette langue. Le livre est agrémenté de textes anglais, traitant de quelques découvertes ou expériences intéressantes. Des thèmes sont prévus qui doivent permettre à l'ètudiant "de faire le point dans ses études littéraires". Celles-ci peuvent – selon l'auteur – facilement être menées à bien, moyennant un petit travail personnel de 3 heures par semaine. A recommander.

P. DE BIEVRE (Gand)

SOME QUANTITATIVE REMARKS ON EXTRACTION EQUILIBRIA. II

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In a previous paper[1] we derived two expressions for the extraction of a metal ion as a chelate:

$$\mathrm{R}^- = \frac{K^a_{\mathrm{HR}} \cdot K_w \cdot f \cdot B}{K_w \mathrm{H}^+ (f + E_{\mathrm{HR}}) + f\{K^b_{\mathrm{HR}} (\mathrm{H}^+)^2 + K^a_{\mathrm{HR}} K_w\}} \qquad \text{(A)}$$

and

$$\frac{m^{+n}\ \text{res.}}{a} = \frac{f \cdot L_{\mathrm{MR}_n}}{\mathrm{MR}_{no}\ \text{sat.}(\mathrm{R}^-)^n + f \cdot L_{\mathrm{MR}_n}} \qquad \text{(B)}$$

We shall now prove the validity of these expressions and show that they correctly predict the behaviour of metal ions in extraction procedures.

Calculation of R^-

It has proved very helpful to work out the value of R^- in the form of a table. From equation A we see that the value of R^- depends on the choice of the system (K^a_{HR}, K^b_{HR}, E_{HR}) and on the conditions used (B, f, H^+).

Initially, only the system oxine – water – chloroform will be considered. Of the conditions, f is taken as 5, hence only extractions in which the volume of the chloroform phase is one-fifth of that of the aqueous phase will be dealt with.

The relationship between B and R^- is linear; accordingly, the R^--table is calculated for a value $B = 1$, and the value of R^- found in the table need only be multiplied by the actual value of B. Thus the tabular values of R^- represent the concentration of oxinate anions in the aqueous phase of a system which contains 1 mg mole of oxine per ml of aqueous phase, and which is in equilibrium with a quantity of chloroform equal to one fifth of the volume of the aqueous phase.

The H^+-concentration is considered as the auto-variant. The values of K_w, K^a_{HR}, K^b_{HR} and E_{HR} are required. The value of K_w is well-known; the figure $1.0 \cdot 10^{-14}$ will be used.

Many data have been published regarding the dissociation constants of oxine. Fox[2] found the value $K^a_{\mathrm{HR}} = 3.68 \cdot 10^{-11}$ from hydrolysis measurements. STONE AND FRIEDMAN[3], using the solubility method of DAVIDSON[4], found values between

$4.20 \cdot 10^{-11}$ and $4.28 \cdot 10^{-11}$. PHILIPS AND MERRIT[5], using the optical method of STENSTROM AND GOLDSMITH[6], found $pK^a_{HR} = 9.70$ ($K^a_{HR} = 1.95 \cdot 10^{-10}$) and $pK^b_{HR} = 9.08$ ($K^b_{HR} = 8.32 \cdot 10^{-10}$). From potentiometric titrations BORREL AND PÂRIS[7] found $pK^a_{HR} = 9.85$ and p"K^b_{HR}"$= 5.05$. This "K^b_{HR}" is not the same as "our" K^b_{HR}, but is related to it by the simple equation: K^b_{HR} (our definition) $= K_w/$"K^b_{HR}", and accordingly $pK^b_{HR} = 8.95$. BOCQUET AND PÂRIS[8], comparing potentiometric and optical methods, found $pK^a_{HR} = 9.82$ and p"K^b_{HR}" $= 5.10$. In good agreement are also the values $pK^a_{HR} = 9.82$ and $pK^b_{HR} = 5.09$ found by LACROIX[9]. UMLAND AND PUCHELT[10] found $pK^a_{HR} = 9.60$ and p"K^b_{HR}" $= 5.33$, by extracting oxine with benzene at various pH-values. These values are based on the determination of the partition coefficient and therefore are as inaccurate as the bromatometric determination of 11 μg of oxine in 50 ml of aqueous solution.

The values $K^a_{HR} = 1.3 \cdot 10^{-10}$ and $K^b_{HR} = 1.2 \cdot 10^{-9}$, will be used here; these are based on earlier work[7-9].

For the partition coefficient of oxine between water and chloroform values of 720[9] and 350[11] have been given. These values disagree, hence the determination of the value of E_{HR} was repeated.

A quantity of oxine was weighed exactly and shaken for 20 h with chloroform and an aqueous buffer solution. The volumes of both phases were determined. In the aqueous phase the pH was measured and the sum of undissociated oxine and oxinate ion was determined by bromatometric titration.

With the known value of K^a_{HR}, the concentration of undissociated oxine was calculated. The term K^b_{HR} was neglected, which is allowed at the pH values considered.

The quantity of oxine in the chloroform phase was obtained from the difference between the amount of oxine taken and the amount of oxine + oxinate found in the aqueous phase.

In the first experiment, 346.2 mg of oxine (2.387 mg moles) were shaken in a glass-stoppered measuring cylinder with aqueous buffer and chloroform and the layers were allowed to separate; the volumes of aqueous and chloroform phases were 33.5 and 25 ml respectively.

The pH of the aqueous phase, measured with a glass electrode, was 8.71, thus $H^+ = 2 \cdot 10^{-9}$.

To 20 ml of the aqueous phase 3.18 ml of 0.1004 N bromate solution, 250 mg of potassium bromide and 5 ml of 6 N HCl were added. The excess of bromate was back-titrated with 2.81 ml of 0.1000 N thiosulphate.

The aqueous phase thus contained 0.0644 mg equivs. or 0.0161 mg moles of oxine + oxinate.

$$Ox^- + HOx = 0.0161 \qquad (1)$$

$$K^a_{HR} = \frac{H^+ \cdot Ox^-}{HOx} = 1.3 \cdot 10^{-10},$$

$$2.10^{-9} \cdot Ox^- = 1.3 \cdot 10^{-10}\, HOx$$

$$\text{or } Ox^- = 0.065\, HOx \qquad (2)$$

TABLE I

pH	R^-	$(R^-)^2$	$(R^-)^3$
1.0	$1.1 \cdot 10^{-13}$	$1.2 \cdot 10^{-26}$	$1.3 \cdot 10^{-39}$
1.1	$1.7 \cdot 10^{-13}$	$2.9 \cdot 10^{-26}$	$4.9 \cdot 10^{-39}$
1.2	$2.7 \cdot 10^{-13}$	$7.3 \cdot 10^{-26}$	$2.0 \cdot 10^{-38}$
1.3	$4.3 \cdot 10^{-13}$	$1.8 \cdot 10^{-25}$	$8.0 \cdot 10^{-38}$
1.4	$6.5 \cdot 10^{-13}$	$4.2 \cdot 10^{-25}$	$2.7 \cdot 10^{-37}$
1.5	$1.1 \cdot 10^{-12}$	$1.2 \cdot 10^{-24}$	$1.3 \cdot 10^{-36}$
1.6	$1.7 \cdot 10^{-12}$	$2.9 \cdot 10^{-24}$	$4.9 \cdot 10^{-36}$
1.7	$2.7 \cdot 10^{-12}$	$7.3 \cdot 10^{-24}$	$2.0 \cdot 10^{-35}$
1.8	$4.1 \cdot 10^{-12}$	$1.7 \cdot 10^{-23}$	$6.9 \cdot 10^{-35}$
1.9	$6.5 \cdot 10^{-12}$	$4.2 \cdot 10^{-23}$	$2.7 \cdot 10^{-34}$
2.0	$1.0 \cdot 10^{-11}$	$1.0 \cdot 10^{-22}$	$1.0 \cdot 10^{-33}$
2.1	$1.6 \cdot 10^{-11}$	$2.6 \cdot 10^{-22}$	$4.1 \cdot 10^{-33}$
2.2	$2.6 \cdot 10^{-11}$	$6.8 \cdot 10^{-22}$	$1.8 \cdot 10^{-32}$
2.3	$4.1 \cdot 10^{-11}$	$1.7 \cdot 10^{-21}$	$6.9 \cdot 10^{-32}$
2.4	$5.9 \cdot 10^{-11}$	$3.5 \cdot 10^{-21}$	$2.1 \cdot 10^{-31}$
2.5	$9.8 \cdot 10^{-11}$	$9.6 \cdot 10^{-21}$	$9.4 \cdot 10^{-31}$
2.6	$1.5 \cdot 10^{-10}$	$2.3 \cdot 10^{-20}$	$3.4 \cdot 10^{-30}$
2.7	$2.3 \cdot 10^{-10}$	$5.3 \cdot 10^{-20}$	$1.2 \cdot 10^{-29}$
2.8	$3.4 \cdot 10^{-10}$	$1.2 \cdot 10^{-19}$	$3.9 \cdot 10^{-29}$
2.9	$5.0 \cdot 10^{-10}$	$2.5 \cdot 10^{-19}$	$1.3 \cdot 10^{-28}$
3.0	$8.0 \cdot 10^{-10}$	$6.4 \cdot 10^{-19}$	$5.1 \cdot 10^{-28}$
3.1	$1.2 \cdot 10^{-9}$	$1.4 \cdot 10^{-18}$	$1.7 \cdot 10^{-27}$
3.2	$1.8 \cdot 10^{-9}$	$3.2 \cdot 10^{-18}$	$5.8 \cdot 10^{-27}$
3.3	$2.5 \cdot 10^{-9}$	$6.3 \cdot 10^{-18}$	$1.6 \cdot 10^{-26}$
3.4	$3.6 \cdot 10^{-9}$	$1.3 \cdot 10^{-17}$	$4.7 \cdot 10^{-26}$
3.5	$5.0 \cdot 10^{-9}$	$2.5 \cdot 10^{-17}$	$1.3 \cdot 10^{-25}$
3.6	$7.1 \cdot 10^{-9}$	$5.0 \cdot 10^{-17}$	$3.6 \cdot 10^{-25}$
3.7	$9.8 \cdot 10^{-9}$	$9.6 \cdot 10^{-17}$	$9.4 \cdot 10^{-25}$
3.8	$1.3 \cdot 10^{-8}$	$1.7 \cdot 10^{-16}$	$2.2 \cdot 10^{-24}$
3.9	$1.8 \cdot 10^{-8}$	$3.2 \cdot 10^{-16}$	$5.8 \cdot 10^{-24}$
4.0	$2.4 \cdot 10^{-8}$	$5.8 \cdot 10^{-16}$	$1.4 \cdot 10^{-23}$
4.1	$3.1 \cdot 10^{-8}$	$9.6 \cdot 10^{-16}$	$3.0 \cdot 10^{-23}$
4.2	$4.3 \cdot 10^{-8}$	$1.8 . 10^{-15}$	$8.0 \cdot 10^{-23}$
4.3	$5.0 \cdot 10^{-8}$	$2.5 \cdot 10^{-15}$	$1.3 \cdot 10^{-22}$
4.4	$6.9 \cdot 10^{-8}$	$4.8 \cdot 10^{-15}$	$3.3 \cdot 10^{-22}$
4.5	$9.0 \cdot 10^{-8}$	$8.1 \cdot 10^{-15}$	$7.3 \cdot 10^{-22}$
4.6	$1.1 \cdot 10^{-7}$	$1.2 \cdot 10^{-14}$	$1.3 \cdot 10^{-21}$
4.7	$1.5 \cdot 10^{-7}$	$2.3 \cdot 10^{-14}$	$3.4 \cdot 10^{-21}$
4.8	$1.9 \cdot 10^{-7}$	$3.6 \cdot 10^{-14}$	$6.9 \cdot 10^{-21}$
4.9	$2.4 \cdot 10^{-7}$	$5.8 \cdot 10^{-14}$	$1.4 \cdot 10^{-20}$
5.0	$3.0 \cdot 10^{-7}$	$9.0 \cdot 10^{-14}$	$2.7 \cdot 10^{-20}$
5.1	$3.8 \cdot 10^{-7}$	$1.4 \cdot 10^{-13}$	$5.5 \cdot 10^{-20}$
5.2	$5.0 \cdot 10^{-7}$	$2.5 \cdot 10^{-13}$	$1.3 \cdot 10^{-19}$
5.3	$6.0 \cdot 10^{-7}$	$3.6 \cdot 10^{-13}$	$2.2 \cdot 10^{-19}$
5.4	$7.6 \cdot 10^{-7}$	$5.8 \cdot 10^{-13}$	$4.4 \cdot 10^{-19}$
5.5	$9.7 \cdot 10^{-7}$	$9.4 \cdot 10^{-13}$	$9.1 \cdot 10^{-19}$
5.6	$1.2 \cdot 10^{-6}$	$1.4 \cdot 10^{-12}$	$1.7 \cdot 10^{-18}$
5.7	$1.5 \cdot 10^{-6}$	$2.3 \cdot 10^{-12}$	$3.4 \cdot 10^{-1}$
5.8	$2.0 \cdot 10^{-6}$	$4.0 \cdot 10^{-12}$	$8.0 \cdot 10^{-18}$
5.9	$2.5 \cdot 10^{-6}$	$6.3 \cdot 10^{-12}$	$1.6 \cdot 10^{-17}$
6.0	$3.1 \cdot 10^{-6}$	$9.6 \cdot 10^{-12}$	$3.0 \cdot 10^{-17}$
6.1	$3.8 \cdot 10^{-6}$	$1.4 \cdot 10^{-11}$	$5.5 \cdot 10^{-17}$
6.2	$5.0 \cdot 10^{-6}$	$2.5 \cdot 10^{-11}$	$1.3 \cdot 10^{-16}$
6.3	$6.0 \cdot 10^{-6}$	$3.6 \cdot 10^{-11}$	$2.2 \cdot 10^{-16}$
6.4	$7.7 \cdot 10^{-6}$	$5.9 \cdot 10^{-11}$	$4.6 \cdot 10^{-16}$
6.5	$9.8 \cdot 10^{-6}$	$9.6 \cdot 10^{-11}$	$9.4 \cdot 10^{-16}$
6.6	$1.2 \cdot 10^{-5}$	$1.4 \cdot 10^{-10}$	$1.7 \cdot 10^{-15}$
6.7	$1.5 \cdot 10^{-5}$	$2.3 \cdot 10^{-10}$	$3.4 \cdot 10^{-15}$
6.8	$2.0 \cdot 10^{-5}$	$4.0 \cdot 10^{-10}$	$8.0 \cdot 10^{-15}$
6.9	$2.5 \cdot 10^{-5}$	$6.3 \cdot 10^{-10}$	$1.6 \cdot 10^{-14}$

TABLE I (continued)

pH	R^-	$(R^-)^2$	$(R^-)^3$	pH	R^-	$(R^-)^2$	$(R^-)^3$
7.0	$3.1 \cdot 10^{-5}$	$9.6 \cdot 10^{-10}$	$3.0 \cdot 10^{-14}$	10.0	$3.0 \cdot 10^{-2}$	$9.0 \cdot 10^{-4}$	$2.7 \cdot 10^{-5}$
7.1	$3.8 \cdot 10^{-5}$	$1.4 \cdot 10^{-9}$	$5.5 \cdot 10^{-14}$	10.1	$3.6 \cdot 10^{-2}$	$1.3 \cdot 10^{-3}$	$4.7 \cdot 10^{-5}$
7.2	$5.0 \cdot 10^{-5}$	$2.5 \cdot 10^{-9}$	$1.3 \cdot 10^{-13}$	10.2	$4.6 \cdot 10^{-2}$	$2.1 \cdot 10^{-3}$	$9.7 \cdot 10^{-5}$
7.3	$6.0 \cdot 10^{-5}$	$3.6 \cdot 10^{-9}$	$2.2 \cdot 10^{-13}$	10.3	$5.4 \cdot 10^{-2}$	$2.9 \cdot 10^{-3}$	$1.6 \cdot 10^{-4}$
7.4	$7.7 \cdot 10^{-5}$	$5.9 \cdot 10^{-9}$	$4.6 \cdot 10^{-13}$	10.4	$7.1 \cdot 10^{-2}$	$5.0 \cdot 10^{-3}$	$3.6 \cdot 10^{-4}$
7.5	$9.8 \cdot 10^{-5}$	$9.6 \cdot 10^{-9}$	$4.9 \cdot 10^{-13}$	10.5	$8.9 \cdot 10^{-2}$	$7.9 \cdot 10^{-3}$	$7.0 \cdot 10^{-4}$
7.6	$1.2 \cdot 10^{-4}$	$1.4 \cdot 10^{-8}$	$1.7 \cdot 10^{-12}$	10.6	$1.1 \cdot 10^{-1}$	$1.2 \cdot 10^{-2}$	$1.3 \cdot 10^{-3}$
7.7	$1.5 \cdot 10^{-4}$	$2.3 \cdot 10^{-8}$	$3.4 \cdot 10^{-12}$	10.7	$1.3 \cdot 10^{-1}$	$1.7 \cdot 10^{-2}$	$2.2 \cdot 10^{-3}$
7.8	$2.0 \cdot 10^{-4}$	$4.0 \cdot 10^{-8}$	$8.0 \cdot 10^{-12}$	10.8	$1.6 \cdot 10^{-1}$	$2.6 \cdot 10^{-2}$	$4.1 \cdot 10^{-3}$
7.9	$2.5 \cdot 10^{-4}$	$6.3 \cdot 10^{-8}$	$1.6 \cdot 10^{-11}$	10.9	$2.0 \cdot 10^{-1}$	$4.0 \cdot 10^{-2}$	$8.0 \cdot 10^{-3}$
8.0	$3.1 \cdot 10^{-4}$	$9.6 \cdot 10^{-8}$	$3.0 \cdot 10^{-11}$	11.0	$2.3 \cdot 10^{-1}$	$5.3 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$
8.1	$3.8 \cdot 10^{-4}$	$1.4 \cdot 10^{-7}$	$5.5 \cdot 10^{-11}$	11.1	$2.7 \cdot 10^{-1}$	$7.3 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$
8.2	$5.0 \cdot 10^{-4}$	$2.5 \cdot 10^{-7}$	$1.3 \cdot 10^{-10}$	11.2	$3.3 \cdot 10^{-1}$	$1.1 \cdot 10^{-1}$	$3.6 \cdot 10^{-2}$
8.3	$6.0 \cdot 10^{-4}$	$3.6 \cdot 10^{-7}$	$2.2 \cdot 10^{-10}$	11.3	$3.6 \cdot 10^{-1}$	$1.3 \cdot 10^{-1}$	$4.7 \cdot 10^{-2}$
8.4	$7.7 \cdot 10^{-4}$	$5.9 \cdot 10^{-7}$	$4.6 \cdot 10^{-10}$	11.4	$4.3 \cdot 10^{-1}$	$1.8 \cdot 10^{-1}$	$8.0 \cdot 10^{-2}$
8.5	$9.8 \cdot 10^{-4}$	$9.6 \cdot 10^{-7}$	$9.4 \cdot 10^{-10}$	11.5	$5.0 \cdot 10^{-1}$	$2.5 \cdot 10^{-1}$	$1.3 \cdot 10^{-1}$
8.6	$1.2 \cdot 10^{-3}$	$1.4 \cdot 10^{-6}$	$1.7 \cdot 10^{-9}$	11.6	$5.4 \cdot 10^{-1}$	$2.9 \cdot 10^{-1}$	$1.6 \cdot 10^{-1}$
8.7	$1.5 \cdot 10^{-3}$	$2.3 \cdot 10^{-6}$	$3.4 \cdot 10^{-9}$	11.7	$5.9 \cdot 10^{-1}$	$3.5 \cdot 10^{-1}$	$2.1 \cdot 10^{-1}$
8.8	$2.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-6}$	$8.0 \cdot 10^{-9}$	11.8	$6.6 \cdot 10^{-1}$	$4.4 \cdot 10^{-1}$	$2.9 \cdot 10^{-1}$
8.9	$2.5 \cdot 10^{-3}$	$6.3 \cdot 10^{-6}$	$1.6 \cdot 10^{-8}$	11.9	$7.1 \cdot 10^{-1}$	$5.0 \cdot 10^{-1}$	$3.6 \cdot 10^{-1}$
9.0	$3.1 \cdot 10^{-3}$	$9.6 \cdot 10^{-6}$	$3.0 \cdot 10^{-8}$	12.0	$7.6 \cdot 10^{-1}$	$5.8 \cdot 10^{-1}$	$4.4 \cdot 10^{-1}$
9.1	$3.8 \cdot 10^{-3}$	$1.4 \cdot 10^{-5}$	$5.5 \cdot 10^{-8}$	12.1	$7.9 \cdot 10^{-1}$	$6.2 \cdot 10^{-1}$	$4.9 \cdot 10^{-1}$
9.2	$5.0 \cdot 10^{-3}$	$2.5 \cdot 10^{-5}$	$1.3 \cdot 10^{-7}$	12.2	$8.3 \cdot 10^{-1}$	$6.9 \cdot 10^{-1}$	$5.7 \cdot 10^{-1}$
9.3	$6.0 \cdot 10^{-3}$	$3.6 \cdot 10^{-5}$	$2.2 \cdot 10^{-7}$	12.3	$8.6 \cdot 10^{-1}$	$7.4 \cdot 10^{-1}$	$6.4 \cdot 10^{-1}$
9.4	$7.6 \cdot 10^{-3}$	$5.8 \cdot 10^{-5}$	$4.4 \cdot 10^{-7}$	12.4	$8.9 \cdot 10^{-1}$	$7.9 \cdot 10^{-1}$	$7.0 \cdot 10^{-1}$
9.5	$9.7 \cdot 10^{-3}$	$9.4 \cdot 10^{-5}$	$9.1 \cdot 10^{-7}$	12.5	$9.0 \cdot 10^{-1}$	$8.1 \cdot 10^{-1}$	$7.3 \cdot 10^{-1}$
9.6	$1.2 \cdot 10^{-2}$	$1.4 \cdot 10^{-4}$	$1.7 \cdot 10^{-6}$	12.6	$9.3 \cdot 10^{-1}$	$8.6 \cdot 10^{-1}$	$8.0 \cdot 10^{-1}$
9.7	$1.5 \cdot 10^{-2}$	$2.3 \cdot 10^{-4}$	$3.4 \cdot 10^{-6}$	12.7	$9.4 \cdot 10^{-1}$	$8.8 \cdot 10^{-1}$	$8.3 \cdot 10^{-1}$
9.8	$1.9 \cdot 10^{-2}$	$3.6 \cdot 10^{-4}$	$6.9 \cdot 10^{-6}$	12.8	$9.6 \cdot 10^{-1}$	$9.2 \cdot 10^{-1}$	$8.8 \cdot 10^{-1}$
9.9	$2.4 \cdot 10^{-2}$	$5.8 \cdot 10^{-4}$	$1.4 \cdot 10^{-5}$	12.9	$9.6 \cdot 10^{-1}$	$9.3 \cdot 10^{-1}$	$9.0 \cdot 10^{-1}$
				13.0	$9.7 \cdot 10^{-1}$	$9.4 \cdot 10^{-1}$	$9.1 \cdot 10^{-1}$

From (1) and (2),

$$1.065 \text{ HOx} = 0.0161 \text{ or HOx} = 0.0151 \text{ mg moles.}$$

and the concentration is therefore 0.00045 mg mole/ml.

The chloroform phase contained 2.387 — 0.016 = 2.371 mg moles of oxine and so its concentration was 0.0948 mg moles/ml.

From these data,

$$E = \frac{\text{concn. HOx in chloroform}}{\text{concn. HOx in water}} = \frac{0.0948}{0.00045} = 211.$$

When the experiment was repeated, the values $E = 210$ and $E = 194$ were found at pH 9.04 and 9.62 respectively.

In the following calculations the mean value $E = 205$ is used. It is not clear why three investigators have found such divergent values.

The results of the calculations of R^- as a function of H^+ are given in Table I. As this has proved to be useful when dealing with bi- and trivalent metal ions, the values of $(R^-)^2$ and $(R^-)^3$ are also included.

Checking of the equations

To check the validity of our equations and the suppositions on which they are based, we have used the extractions of copper and nickel with oxine and chloroform.

Copper–oxine–chloroform

For the expression

$$\frac{m^{+n} \text{ res.}}{a} = \frac{fL_{MR_n}}{MR_{n\,o} \text{ sat.} (R^-)^n + fL_{MR_n}}$$

the values of L_{MR_n} and $MR_{n\,o}$ sat. are still required.

The value of L_{MR_n} is given by BORREL AND PÂRIS[7] as $5 \cdot 10^{-29}$. The value of $7.4 \cdot 10^{-10}$ found by TREADWELL AND AMMAN[12] is incorrect. This value was calculated from the solubility of copper oxinate in 1 *N* acetic acid without considering the amphoteric character of oxine; accordingly, it is too large.

The value of $CuOx_2$ sat. chloroform was determined by shaking chloroform for 24 h with pure copper oxinate, distilling the chloroform, destroying the organic matter with sulphuric–perchloric acids in the presence of ammonium vanadate[14], and by final gravimetric determination of copper.

The value $3.4 \cdot 10^{-3}$ mg moles/ml was found.

The experimental extraction error

In a separatory funnel were placed 49 ml of water*, 1 ml of a copper sulphate solution containing 1 mg Cu/ml, 1 ml of chloroform containing 56.2 mg of oxine/ml, 9 ml of chloroform* and a few drops of 2 *N* hydrochloric acid. The stoppered funnel was shaken for 5 × 2 min, with 2 min between each shaking period. After final separation of the layers, the pH of the aqueous layer was determined as well as the copper content of the chloroform layer and in some cases, the copper content of the aqueous layer.

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* In order to avoid large changes of volume of the phases, the water and the chloroform used were saturated with chloroform and water respectively.

Copper was determined in the chloroform layer by measuring the absorbance at 450 mμ. A standard curve was prepared by dissolving a weighed amount of pure copper oxinate in chloroform and measuring the absorbance at 450 mμ of known dilutions of this solution.

Copper was determined in the aqueous layer with rubeanic acid[13] after destruction of organic matter with sulphuric–perchloric acids in the presence of ammonium vanadate[14]. The results are given in Table II.

TABLE II

pH	*aqueous phase*	*chloroform phase*	
	mg of copper rubeanic acid	*mg of copper*	
		as oxinate	*rubeanic acid*
1.64		< 0.01	
1.96		0.04	
2.10		0.19	
2.12		0.14	
2.20		0.26	0.28
2.25	0.61	0.37	
2.36	0.36	0.64	0.68
2.50	0.21		0.86
2.55	0.09		
2.85	< 0.01		
3.04	< 0.01		

The calculated extraction error

In our experiments the value of B (defined as b/V_w) was $^{56.2}/_{145} \cdot {^1}/_{50} = 8.10^{-3}$, hence the values of $(R^-)^2$ found in Table I must be multiplied by $B^2 = 6.4 \cdot 10^{-5}$. Only

TABLE III

pH	$(R^-)^2_{n=1}$	$(R^-)^2_{n=8.10^{-3}}$	$CuOx_2$ *sat.* $(R^-)^2$	$f\,L_{CuOx_2}$	$\frac{m^{+2}\ res.}{a}$
1.6	$2.9 \cdot 10^{-24}$	$1.8 \cdot 10^{-28}$	$6.1 \cdot 10^{-31}$	$2.5 \cdot 10^{-28}$	1.00
1.7	$7.3 \cdot 10^{-24}$	$4.7 \cdot 10^{-28}$	$1.6 \cdot 10^{-30}$		1.00
1.8	$1.7 \cdot 10^{-23}$	$1.1 \cdot 10^{-27}$	$3.7 \cdot 10^{-30}$		1.00
1.9	$4.2 \cdot 10^{-23}$	$2.7 \cdot 10^{-27}$	$9.2 \cdot 10^{-30}$		0.96
2.0	$1.0 \cdot 10^{-22}$	$6.4 \cdot 10^{-27}$	$2.2 \cdot 10^{-29}$		0.93
2.1	$2.6 \cdot 10^{-22}$	$1.7 \cdot 10^{-26}$	$5.8 \cdot 10^{-29}$		0.81
2.2	$6.8 \cdot 10^{-22}$	$4.4 \cdot 10^{-26}$	$1.5 \cdot 10^{-28}$		0.63
2.3	$1.7 \cdot 10^{-21}$	$1.1 \cdot 10^{-25}$	$3.7 \cdot 10^{-28}$		0.40
2.4	$3.5 \cdot 10^{-21}$	$2.2 \cdot 10^{-25}$	$7.5 \cdot 10^{-28}$		0.25
2.5	$9.6 \cdot 10^{-21}$	$6.1 \cdot 10^{-25}$	$2.1 \cdot 10^{-27}$		0.11
2.6	$2.3 \cdot 10^{-20}$	$1.5 \cdot 10^{-24}$	$5.1 \cdot 10^{-27}$		0.04
2.7	$5.3 \cdot 10^{-20}$	$3.4 \cdot 10^{-24}$	$1.2 \cdot 10^{-26}$		0.02
2.8	$1.2 \cdot 10^{-19}$	$7.7 \cdot 10^{-24}$	$2.6 \cdot 10^{-26}$		0.01
2.9	$2.5 \cdot 10^{-19}$	$1.6 \cdot 10^{-23}$	$5.4 \cdot 10^{-26}$		0.005
3.0	$6.4 \cdot 10^{-19}$	$4.1 \cdot 10^{-23}$	$1.4 \cdot 10^{-25}$		0.002

the pH range of 1.6 to 3.0 will be considered. From the values of $(R^-)^2$ obtained, the values of

$$\frac{m^{+2}\text{res.}}{a} = \frac{fL_{MR_2}}{MR_{2\,o}\,\text{sat.}\,(R^-)^2 + fL_{MR_2}}$$

can be calculated (Table III).

The experimental and the calculated values are shown in Fig. 1, curve I.

The experiments were repeated with a smaller amount of oxine ($B = 4.3 \cdot 10^{-3}$). The results as well as the calculated values are shown in Fig. 1, curve II.

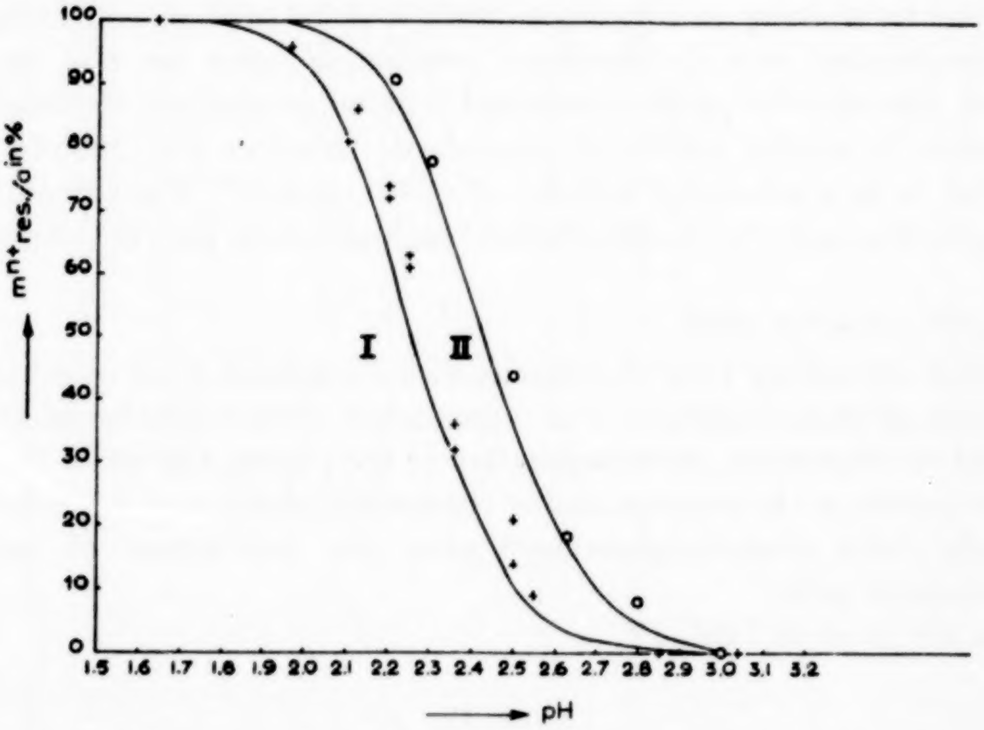

Fig. 1. The extraction of copper with oxine and chloroform as a function of pH.
Curve I. Calculated extraction error $B = 8 \cdot 10^{-3}$. + = experimentally found extraction error.
Curve II. Calculated extraction error $B = 4.3 \cdot 10^{-3}$. o = experimentally found extraction error.

Nickel–oxine–chloroform

The values of f, B, A and n, which depend only on the conditions chosen can be calculated in the same way as in the experiments with copper–oxine–chloroform. The values of K_w, K^a_{HR}, K^b_{HR} and E_{HR} are also the same, of course.

For the solubility product of nickel oxinate, IRVING AND WILLIAMS[15] found a value of $7.9 \cdot 10^{-23}$. From the experimental data of BORREL AND PÂRIS[7], a value of $7 \cdot 10^{-23}$ can be calculated, and this is used in the following calculations.

The solubility of nickel oxinate in chloroform was determined by shaking pure nickel oxinate for 24 h and determining the nickel in the solution. This solubility proved to be nil, hence it would seem that no extraction is possible. Nevertheless, this extraction has been published[15-18]. Surprisingly, when a nickel solution (pH = 6) is shaken with a solution of oxine in chloroform a definite extraction is obtained. The chloroform solutions, however, are very unstable, nickel oxinate precipitates and after a short time the chloroform is free of nickel.

It can be assumed that the undissociated but not yet precipitated nickel oxinate is extracted from the aqueous phase, and forms chloroform-insoluble $NiOx_2 \cdot 2$ aq with the water dissolved in the chloroform. UMLAND AND HOFFMANN[19] found that chloroform solutions of metal oxinates were stabilized by the addition of polar organic compounds, *n*-butylamine being one of the most effective. It is supposed that the *n*-butylamine replaces the water in an equilibrium:

$$NiOx_2 \cdot 2H_2O + 2\text{ b.a.} \rightleftarrows NiOx_2 \cdot 2\text{ b.a.} + 2H_2O$$

in which b.a. is written for *n*-butylamine. The compound $NiOx_2 \cdot 2$ b.a. is soluble in chloroform.

The solubility of nickel oxinate was therefore determined in chloroform in presence of *n*-butylamine by shaking an aqueous solution of nickel sulphate containing a large excess of *n*-butylamine with a chloroform solution of oxine for 8 h. At the end of this period, the aqueous phase contained a green precipitate of nickel oxinate which proved to be readily soluble in chloroform, therefore the chloroform phase was considered to be a saturated solution of nickel oxinate*. The concentration of nickel oxinate in this perfectly stable solution was found to be $5.0 \cdot 10^{-2}$ mg moles/ml.

The experimental extraction error

50 ml of water containing 1 mg of nickel as nickel sulphate, 1 ml of *n*-butylamine and a few drops of dilute sulphuric acid were shaken with a solution of 49.5 mg of oxine in 10 ml of chloroform. After separation of the phases, the pH of the aqueous phase was measured; in the aqueous and/or chloroform phase, nickel was determined colorimetrically with dimethylglyoxime[20] after the destruction of oxine with sulphuric–perchloric acids.

The results are given in Table IV.

TABLE IV

pH	*aqueous phase mg of nickel*	*chloroform phase mg of nickel*
2.91	1.00	0.02
3.10	0.96	0.03
3.16		0.10
3.40	0.56	
3.60	0.25	0.74
3.79	0.09	
4.03	0.03	
4.66	0.00	1.00
6.47	0.00	1.02

The calculated extraction error

From the values $L_{NiOx_2} = 7 \cdot 10^{-23}$, $NiOx_2$ sat. chloroform $= 5 \cdot 10^{-2}$, R^- from Table I, using $B = 49.5/145 \cdot 1/50 = 6.8 \cdot 10^{-3}$, the extraction error can be calculated.

The calculations are shown in Table V.

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* We consider the reaction: $NiOx_2 + 2\text{ b.a.} \rightarrow NiOx_2 \cdot 2\text{ b.a.}$ a secondary one, which is of no importance for our purposes.

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TABLE V

pH	$(R^-)^2_{B=1}$	$(R^-)^2_{B=6.8\cdot10^{-3}}$	$NiOx_2\ sat.(R^-)_2$	fL_{NiOx_2}	$\frac{m^{+2}\ res.}{a}$
2.7	$5.3\cdot10^{-20}$	$2.5\cdot10^{-24}$	$1.2\cdot10^{-25}$	$3.5\cdot10^{-23}$	1.00
2.8	$1.2\cdot10^{-19}$	$5.6\cdot10^{-24}$	$2.8\cdot10^{-25}$		0.99
2.9	$2.5\cdot10^{-19}$	$1.2\cdot10^{-23}$	$5.8\cdot10^{-25}$		0.98
3.0	$6.4\cdot10^{-19}$	$3.0\cdot10^{-23}$	$1.5\cdot10^{-24}$		0.96
3.1	$1.4\cdot10^{-18}$	$6.6\cdot10^{-23}$	$3.3\cdot10^{-24}$		0.91
3.2	$3.2\cdot10^{-18}$	$1.5\cdot10^{-22}$	$7.5\cdot10^{-24}$		0.82
3.3	$6.3\cdot10^{-18}$	$3.0\cdot10^{-22}$	$1.5\cdot10^{-23}$		0.70
3.4	$1.3\cdot10^{-17}$	$6.1\cdot10^{-22}$	$3.0\cdot10^{-23}$		0.54
3.5	$2.5\cdot10^{-17}$	$1.2\cdot10^{-21}$	$5.8\cdot10^{-23}$		0.38
3.6	$5.0\cdot10^{-17}$	$2.4\cdot10^{-21}$	$1.2\cdot10^{-22}$		0.23
3.7	$9.6\cdot10^{-17}$	$4.5\cdot10^{-21}$	$2.2\cdot10^{-22}$		0.14
3.8	$1.7\cdot10^{-16}$	$8.0\cdot10^{-21}$	$4.0\cdot10^{-22}$		0.08
3.9	$3.2\cdot10^{-16}$	$1.5\cdot10^{-20}$	$7.5\cdot10^{-22}$		0.04
4.0	$5.8\cdot10^{-16}$	$2.7\cdot10^{-20}$	$1.4\cdot10^{-21}$		0.02
4.1	$9.6\cdot10^{-16}$	$4.5\cdot10^{-20}$	$2.2\cdot10^{-21}$		0.02
4.2	$1.8\cdot10^{-15}$	$8.5\cdot10^{-20}$	$4.2\cdot10^{-21}$		0.01
4.3	$2.5\cdot10^{-15}$	$1.2\cdot10^{-19}$	$5.8\cdot10^{-21}$		0.01
4.4	$4.8\cdot10^{-15}$	$2.3\cdot10^{-19}$	$1.1\cdot10^{-20}$		0.00
4.5	$8.1\cdot10^{-15}$	$3.8\cdot10^{-19}$	$1.9\cdot10^{-20}$		0.00

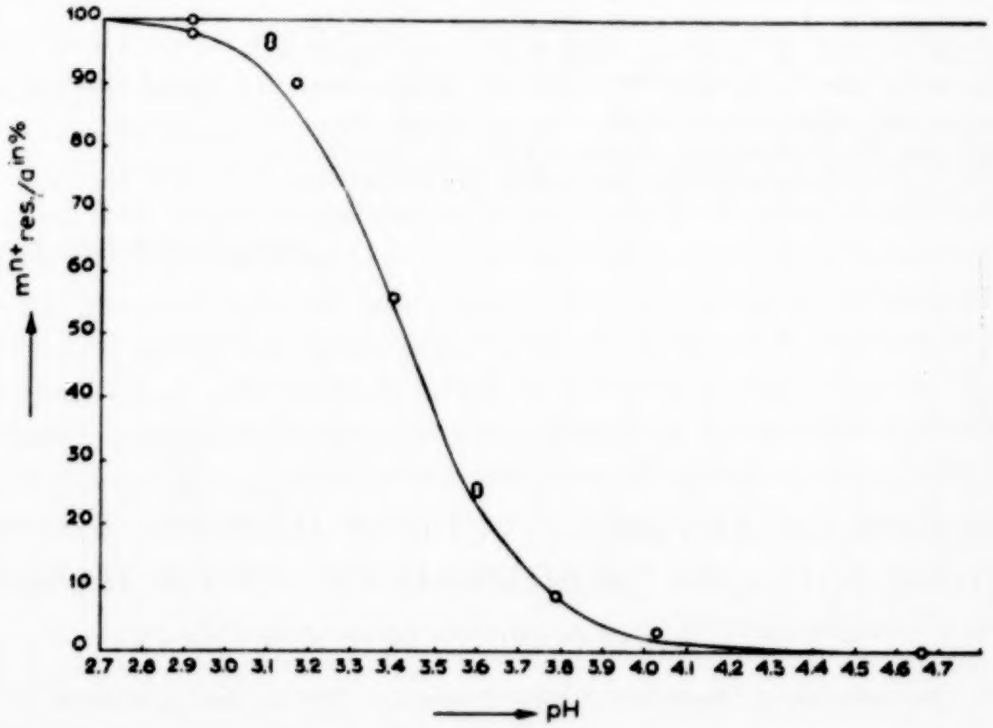

Fig. 2. The extraction of nickel with oxine and chloroform in presence of *n*-butylamine as a function of pH. Calculated and experimentally found extraction errors.

The calculated values and the experimentally found extraction errors are shown in Fig. 2.

It can be concluded that in both systems the course of the extraction is predicted correctly by the equations given in our previous paper[1].

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SUMMARY

The equations given in a previous paper are shown to predict the course of solvent extraction correctly in the case of copper – oxine – chloroform as well as that of nickel – oxine – chloroform. Both pH and quantity of reagent prove to have the effect required by the equations.

RÉSUMÉ

Les équations proposées dans le premier article de cette série ont été appliquées aux cas suivants d'extraction par solvant: cuivre–oxine–chloroform et nickel–oxine–chloroforme.

ZUSAMMENFASSUNG

Mit Hilfe der in einer früheren Veröffentlichung mitgeteilten Gleichungen wurde der Verlauf der Extraktion folgender Systeme verfolgt: Kupfer–Oxin–Chloroform und Nickel–Oxin–Chloroform.

REFERENCES

[1] M. Oosting, *Anal. Chim. Acta*, 21 (1959) 301.
[2] J. J. Fox, *J. Chem. Soc.*, 97 (1910) 1119.
[3] K. G. Stone and L. Friedman, *J. Am. Chem. Soc.*, 69 (1947) 209.
[4] D. Davidson, *J. Chem. Educ.*, 19 (1942) 221.
[5] J. P. Philips and L. L. Merrit, jr., *J. Am. Chem. Soc.*, 70 (1948) 410.
[6] W. Stenstrom and N. Goldsmith, *J. Phys. Chem.*, 30 (1926) 1683.
[7] M. Borrel and R. A. Pâris, *Anal. Chim. Acta*, 6 (1952) 389.
[8] G. Bocquet and R. A. Pâris, *Anal. Chim. Acta*, 14 (1956) 1.
[9] S. Lacroix, *Anal. Chim. Acta*, 1 (1947) 260.
[10] F. Umland and H. Puchelt, *Anal. Chim. Acta*, 16 (1957) 334.
[11] Th. Moeller and F. L. Pundsack, *J. Am. Chem. Soc.*, 75 (1953) 2258.
[12] W. D. Treadwell and A. Amman, *Helv. Chim. Acta*, 21 (1938) 1249.
[13] K. Quandel, *Arch. Eisenhüttenw.*, 14 (1941) 604.
[14] M. Oosting, *Thesis*, Delft, 1958.
[15] H. M. Irving and R. J. P. Williams, *Analyst*, 77 (1952) 813.
[16] O. A. Kenyon and H. A. Bewick, *Anal. Chem.*, 24 (1952) 1826.
[17] L. Silverman, L. Moudy and D. W. Hawley, *Anal. Chem.*, 25 (1953) 1369.
[18] Th. Moeller, *Ind. Eng. Chem., Anal. Ed.*, 15 (1943) 463.
[19] F. Umland and W. Hoffmann, *Angew. Chem.*, 68 (1956) 704.
[20] A. Claassen and L. Bastings, *Rec. trav. chim.*, 73 (1954) 783.

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SEPARATION OF ANTIMONY(V) FROM IRON(III), COPPER(II), COBALT(II) AND CADMIUM(II) BY ION-EXCHANGE

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In view of the difficulties usually associated with the conventional method of separation of antimony by precipitation as sulphide[1], a simpler rapid method was desirable. In a previous communication[2], a solvent extraction method for separating macro quantities of antimony(V) from nickel(II), chromium(III), lead(II), tin (IV), mercury(II) and small amounts of copper(II) was described. Iron(III), cobalt(II), cadmium(II) and large quantities of copper(II) interfered with this method. It has now been found possible to separate these interfering cations from antimony(V) with the help of a cation-exchange resin (Zeo-Carb-225).

Separation of mixtures of antimony and other cations by ion-exchange resins has been reported in a few cases; none of these is useful in solving the present problem. LUR'E AND FILIPPOVA[3] separated zinc, aluminium, molybdenum, tungsten and antimony (from elements, *e.g.* Cu, Fe, which form basic hydroxides) by first adsorbing them all on a cation-exchanger (Wolfatit-P) and then eluting them with caustic soda solution of different concentrations. The same cation-exchanger retained antimony and tin from dilute acid solution but allowed arsenic to pass quantitatively[4]. It was also used for the separation of bismuth from antimony from 6% ammonium thiocyanate solution in 1 N H_2SO_4; this separation was very sensitive to thiocyanate concentration.

Anion-exchange resins have also been used in some cases. SMITH AND REYNOLDS[5] separated tracer quantities of ^{124}Sb(V), ^{113}Sn(IV) and ^{125}Te(IV) by adsorption on a Dowex-1 resin and subsequent elution with 0.1 M oxalic acid followed by M H_2SO_4. More recently, KLEMENT[6] claimed to have effected an excellent separation of arsenate from antimonate (as their soluble potassium salts) by adsorbing the former quantitatively on a strongly basic anion-exchanger in the sulfate form; but a considerable amount of potassium hydroxide had to be used to free the column from antimonate which was collected in the effluent.

In the present case we were concerned mainly with the determination of antimony in insoluble heavy metal antimonates. These can be dissolved in mineral acids, but the high acidity which is necessary to prevent hydrolysis of antimony(V) prevents adsorbtion on a cation exchanger. In presence of a complexing agent for antimony, the excess of mineral acid may be avoided. With a tartaric acid solution, MARCZENKO[7] was able to adsorb copper quantitatively on Wolfatit-P from a mixture with antimony and tin; he reported that 1–3% of antimony was also retained by the resin. Working with Zeo-Carb-225, we have found that retention of antimony(V) depends on the amount of tartaric acid present. With an excess of tartaric acid, copper(II), iron(III), cobalt(II) or cadmium(II) could be completely adsorbed on the resin, with the quantitative exclusion of antimony(V). Based on these observations, a method has been worked out for quantitative separation of antimony from any of the above cations.

EXPERIMENTAL

Antimony stock solution. Approximately 11.0 ml of $SbCl_5$ (B.D.H. reagent) was dissolved in 250 ml of 10% tartaric acid solution (w/v). The solution was filtered and stored in a closed bottle provided with a semi-micro delivery burette. Definite volumes of solution were taken out and their antimony content determined iodometrically.

20% Tartaric acid solution. 50 g of AnalaR tartaric acid was dissolved in 250 ml distilled water.

Solutions containing the other metal ions were prepared from AnalaR or Mercks reagents. The metal contents were verified by conventional methods; copper was determined by the iodometric method, iron by dichromate titration and cobalt and cadmium gravimetrically as their pyridine–thiocyanate complexes.

Solutions for percolation through the resin column were prepared by mixing together definite amounts of antimony stock solution and 20% tartaric acid solution. The mixture was passed through the resin column (Zeo-Carb-225 in H^+ form) at the rate of 30–40 drops per min. The resin column was then washed several times with distilled water and the washings were collected with the effluent, which was analysed for antimony. In the case of mixtures, the solutions were prepared from antimony stock solution, tartaric acid solution and the relevant metal ion solutions. After separation of antimony, the adsorbed cation was eluted by passing hydrochloric acid solutions of known strength through the resin. In the eluate the metals were determined by the methods mentioned above.

RESULTS AND DISCUSSION

Effect of tartaric acid on retention of antimony(V) on Zeo-Carb-225

The effect of varying amounts of tartaric acid on the retention of antimony(V) on the resin can be seen from Table I. As the amount of tartaric acid is increased, retention of antimony(V) on the resin decreases, and with an excess of tartaric acid all the antimony(V) passes through the resin column. The optimum amount of tartaric acid necessary to prevent adsorption of antimony(V) on the resin is 16 to 20 times the weight of the metal.

TABLE I

EFFECT OF TARTARIC ACID CONTENT ON RETENTION OF ANTIMONY(V)

Tartaric acid added g	*Antimony* *taken* g	*Antimony* *found* g	*Antimony retained by resin* %
0.30	0.1115	0.1067	+ 4.30
0.80	0.1115	0.1100	+ 1.345
1.30	0.1115	0.1109	+ 0.54
1.80	0.1115	0.1121	— 0.54
2.30	0.1115	0.1115	0.00
4.60	0.2230	0.2230	0.00
9.20	0.4460	0.4458	+ 0.045

The above results can be explained by considering the formation of stable anionic antimony–tartrate complexes in presence of excess tartaric acid. To support this view, a solution containing 0.1115 g of antimony(V) and 2.30 g of tartaric acid was percolated through an anion-exchanger De-Acidite FF in the sulfate form; the antimony was taken up quantitatively by the resin.

Separation of antimony(V) from interfering cations

Solutions containing known amounts of antimony(V), tartaric acid and varying amounts of one of the interfering elements under study (*viz.* Cu(II), Fe(III), Cd(II) and Co(II)) were percolated through the cation-exchanger, Zeo-Carb-225. The effect of varying the amount of the interfering cation with the tartaric acid and antimony(V) concentrations constant, and the feasibility of quantitative separation were studied. Copper(II), cobalt(II) and cadmium(II) could be quantitatively eluted with 2 *N* hydrochloric acid but iron(III) required 4–6 *N* acid. The results (Tables II–V) indicate that within the range investigated mixtures of antimony(V) with other cations could be satisfactorily analysed; the results were accurate to ± 1%. In all cases, 2.3 g of tartaric acid was used.

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TABLE II

DETERMINATION OF ANTIMONY(V) AND COPPER(II)

Antimony taken g	*Antimony found* g	*Error for antimony* %	*Copper taken* g	*Copper found* g	*Error for copper* %
0.1115	0.1121	+ 0.54	0.03116	0.03116	0.00
0.1115	0.1113	− 0.18	0.06232	0.06169	− 1.01
0.1115	0.1115	0.00	0.12150	0.12020	− 1.07
0.1115	0.1115	0.00	0.24300	0.24240	− 0.25
0.1115	0.1121	+ 0.54	0.48600	0.48600	0.00

TABLE III

DETERMINATION OF ANTIMONY(V) AND IRON(III)

Antimony taken g	*Antimony found* g	*Error for antimony* %	*Iron taken* g	*Iron found* g	*Error for iron* %
0.1115	0.1118	+ 0.27	0.02888	0.02876	− 0.42
0.1115	0.1110	− 0.45	0.05776	0.05752	− 0.42
0.1115	0.1116	+ 0.09	0.11552	0.11610	+ 0.50
0.1115	0.1115	0.00	0.23104	0.23160	+ 0.24
0.1115	0.1121	+ 0.54	0.46208	0.46130	− 0.17

TABLE IV

DETERMINATION OF ANTIMONY(V) AND COBALT(II)

Antimony taken g	*Antimony found* g	*Error for antimony* %	*Cobalt taken* g	*Cobalt found* g	*Error for cobalt* %
0.1115	0.1115	0.00	0.02875	0.02866	− 0.31
0.1115	0.1124	+ 0.81	0.05750	0.05680	− 1.22
0.1115	0.1106	− 0.81	0.11500	0.11540	+ 0.35
0.1115	0.1109	− 0.54	0.23000	0.23110	+ 0.48
0.1115	0.1113	− 0.18	0.46000	0.46280	+ 0.61

TABLE V

DETERMINATION OF ANTIMONY(V) AND CADMIUM(II)

Antimony taken g	*Antimony found* g	*Error for antimony* %	*Cadmium taken* g	*Cadmium found* g	*Error for cadmium* %
0.1115	0.1105	− 0.90	0.0422	0.0413	− 2.13
0.1115	0.1111	− 0.36	0.0844	0.0840	− 0.47
0.1115	0.1118	+ 0.27	0.1688	0.1694	+ 0.36
0.1115	0.1111	− 0.36	0.3376	0.3365	− 0.33
0.1115	0.1118	+ 0.27	0.6752	0.6792	+ 0.59

It was observed that under similar conditions, nickel(II), chromium(III) or lead(II) is also taken up selectively from its mixture with antimony(V) by Zeo-Carb-225, but mercury(II) and tin(II and IV) escape adsorption. As we had earlier found a suitable solvent extraction method[2] for this separation, detailed data on these mixtures are not presented.

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CONCLUSION

The results obtained indicate that in presence of tartaric acid iron(III), cobalt(II), copper(II), cadmium(II), nickel(II), chromium(III) and lead(II) do not form complexes sufficiently stable to escape retention on Zeo-Carb-225 (H^+ form) while antimony(V) forms stable anionic complexes which are not taken up by the resin. Mercury(II), and tin(II and IV) cannot be separated from antimony(V) by this method.

PROPOSED METHOD FOR ANALYSIS OF ANTIMONATES

Decompose 0.20 to 0.40 g of antimonate with conc. hydrochloric acid. Add dilute sodium hydroxide solution to neutralize the acid. Add the calculated amount of tartaric acid (any precipitate first formed must be dissolved completely). Percolate the solution slowly through a Zeo-Carb-225 resin column (10 g resin in H^+ form). Wash the column several times with distilled water and collect the washings with the effluent. Analyse the effluent for antimony by the iodometric method. Elute the cations on the resin with a hydrochloric acid solution of the required strength and analyse the eluate for the metal by conventional methods.

SUMMARY

With excess of tartaric acid, antimony(V) forms a stable anionic complex that completely escapes adsorption on a cation-exchange resin, Zeo-Carb-225, while Cu(II), Fe(III), Co(II) or Cd(II) is quantitatively retained. Antimony(V) can be separated from these ions in this way.

RÉSUMÉ

Une méthode est proposée pour la séparation de l'antimoine(V) d'avec le cuivre, le fer(III), le cobalt et le cadmium, au moyen d'une résine d'échange de cations. L'antimoine doit être complexé au préalable par l'acide tartrique.

ZUSAMMENFASSUNG

Antimon lässt sich in Gegenwart von Weinsäure von Kupfer, Eisen (III), Kobalt und Cadmium mit Hilfe eines sauren Ionenaustauschers abtrennen.

REFERENCES

[1] N. H. FURMAN, *Scott's Standard Methods of Chemical Analysis.* Vol. I. D. Van Nostrand, 5th Ed., New York 1939, page 67.

[2] S. S. M. A. KHORASANI AND M. H. KHUNDKAR, *Anal. Chim. Acta,* 21 (1959) 24.

[3] YU. YU. LUR'E AND N. A. FILIPPOVA, *Zavodskaya Lab.,* 13 (1947) 539.

[4] YU. YU. LUR'E AND N. A. FILIPPOVA, *Zavodskaya Lab.,* 14 (1948) 159.

[5] G. W. SMITH AND S. A. REYNOLDS, *Anal. Chim. Acta,* 12 (1955) 151.

[6] R. KLEMENT, in O. SAMUELSON'S, *Ion-Exchangers in Analytical Chemistry.* John Wiley & Sons Inc., New York 1956, p. 159.

[7] Z. MARCZENKO, *Chem. anal.,* 2 (1957) 255.

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HETEROMETRIC MICRO-DETERMINATION OF TRACES OF IRON IN THIOCYANATE SOLUTIONS BY TITRATION WITH NITRON

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INTRODUCTION

In the present paper a heterometric method is described for a very rapid determination of traces of ferric iron (0.05–0.08 mg in 20 ml of solution) in solutions containing *ca.* 99.9% of the following cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Cr^{+3}, Al^{+3}, Mn^{+2}, Zn^{+2}, Cd^{+2}, Th^{+4} or Ce^{+3}. The same quantity of iron could be determined in the presence of the following ions: Ni^{+2} (∼ 99.8%), Pb^{+2} (99.5%), Sb^{+3} (99.15%), MoO_4^{-2} (99.1%), VO_3^- (98.4%), WO_4^{-2} (96%) and Cu^{+2} (98.7%). A titration usually took *ca.* 5 minutes. In most cases the error was 1% or less, but exceptionally it amounted to *ca.* 3%.

The method is based on the quantitative precipitation of traces of ferric iron in concentrated solutions of thiocyanate by means of nitron.

EXPERIMENTAL

The same working conditions were observed as in previous heterometric investigations. A deep red Corning filter (No. 2408) was always used.

a. A *M* ferric chloride stock solution was prepared from Baker "Analyzed" reagent; this was then gradually diluted with hydrochloric acid solution, so that the latter always had a molarity 10 times higher than that of the iron. The dilute iron solutions were freshly prepared at frequent intervals.

b. An aqueous nitron stock solution (0.01 *M*) was prepared as follows: 0.7802 g of nitron (M.W. 312.16, Eastman Organic Chemicals, for chemical purposes) and 7 ml of *N* acetic acid were dissolved in water to give 250 ml of aqueous solution. The dilute solutions were prepared from this solution every few days. The solutions of nitron were kept in dark brown bottles. The stock solution remained unchanged for months. All other chemicals used were either AnalaR or chemically pure reagents.

RESULTS AND DISCUSSION

In Table I a selection of the experiments is given. A blank experiment was carried out by titrating the concentrated thiocyanate solution with nitron in the absence of iron; a slight white turbidity formed but this never interfered with the titrations. Table I indicates the highest concentration of the foreign metal which may be present without seriously affecting the titration of iron. In all titrations a horizontal maximum density line was obtained (Fig. 1) after the first maximum density point (= end-point). The flocculent precipitate obtained had a brick red colour. The molar ratio of $[Fe^{+3}]$: [N] (N = nitron) at the end-point was always 1 :6.6. The precipitation of small amounts of iron depended on the concentration of thiocyanate in the solution. Thus, practically no precipitation occurred in 0.1 *M* thiocyanate solution

TABLE I

GENERAL COMPOSITION: *a* ml m*M* $FeCl_3$ + *b* ml *N* HCl + *c* ml 2 *M* KCNS + *d* ml supplements + ad 20 ml H_2O + *x* ml *nM* nitron
Content: 0.05–0.084 mg iron. T = 20°. Red filter: Corning No. 2408

Expt. No.	*FeCl₃*		*ml HCl*	*ml KCNS*	*Supplements*	*% Fe*	*Nitron*			*Maximum density value*	*% error*	*Titration time in min.*
	ml	*Molarity*					*Molarity*	*Initial ppt. at ml*	*End-point at ml*			
1	3	0.0005	0.5	1			0.0033	3.8				
2	3	0.0005	0.5	2			0.0033	1.2	i/c 2.90 h	0.46	2.8	10
3	3	0.0005	0.5	3			0.0033	0.6	i 2.94 h	0.68	1.5	5
4	3	0.0005	0.5	5			0.0033	0.6	i/c 3.00 h	0.72	0.5	5
5	3	0.0005	0.5	7			0.0033	0.6	i 3.00 h	0.77	0.5	5
6	3	0.001	0.5	5			0.005	0.0	i 4.00>	>0.95		10
7	4	0.00025	0.5	5			0.0033	0.6	i 2.03 h	0.44	2.0	6
8	3	0.0005	0.5	5			0.0025	1.0	i 4.00 h	0.71	0.5	6
9	3	0.0005	—	5	0.2 ml *M* H_3PO_4		0.0033	0.4	i/c 3.00 h	0.75	0.5	5
10	4	0.0005	—	5	0.5 ml *M* H_3PO_4		0.005	0.6	i 2.70 h	0.81		5
11	4	0.00025	—	5	0.5 ml *M* H_3PO_4		0.0033	0.8	i 2.03 h	0.42	2.0	8
12	3	0.0005	3.5	5	1 ml *M* Na_3-citrate + 5 ml 2 *M* NH_4Cl		0.0033	0.6	i 2.95 h	0.65	1.2	5
13	3	0.0005	3.5	5	1 ml *M* Na_3-citrate + 5 ml 2 *M* NH_4NO_3		0.0033	1.0	i 3.00 h	0.57	0.5	5
14	3	0.0005	5	5	1 ml *M* Na_3-citrate		0.0033	0.6	i 3.01 h	0.62	0.5	5
15	3	0.0005	0.5	5	2 ml *M* $CaCl_2$	0.1	0.0033	0.6	i 3.00 h	0.74	0.5	5
16	3	0.0005	0.5	5	3 ml 3 *M* $AlCl_3$	0.04	0.0033	0.4	i 3.00 h	0.93	0.5	5
17	3	0.0005	0.5	5	5 ml *M* $CrCl_3$	0.04	0.0033	0.4	i 2.98 h	0.57	0.2	4
18	3	0.0005	0.5	5	5 ml 2 *M* $MnCl_2$	0.02	0.0033	0.6	i 3.02 h	0.78	0.7	4
19	3	0.0005	3.5	5	5 ml *M* $CaCl_2$ + 1 ml *M* Na_3-citrate	0.05	0.0033	0.6	i 2.98 h	0.77	0.2	5
20	3	0.0005	3.5	5	5 ml *M* $BaCl_2$ + 1 ml *M* Na_3-citrate	0.02	0.0033	0.4	i 2.98 h	0.76	0.2	5
21	3	0.0005	3.5	5	5 ml 2 *M* $MgCl_2$ + 1 ml *M* Na_3-citrate	0.04	0.0033	0.4	i 2.90 h	0.77	2.8	5
22	3	0.0005	3.5	5	1 ml *M* $Zn(NO_3)_2$ + 1 ml *M* Na_3-citrate	0.15	0.0033	0.2	i 3.10 h	0.53	3.8	7
23	3	0.0005	3.5	5	5 ml *M* $CrCl_3$ + 1 ml *M* Na_3-citrate	0.04	0.0033	0.4	i 3.00 h	0.52	0.5	5
24	3	0.0005	3.5	5	3 ml *M* $Al(NO_3)_3$ + 1 ml *M* Na_3-citrate	0.12	0.0033	0.4	i 3.00 h	0.82	0.5	5
25	3	0.0005	3.5	5	5 ml 2 *M* $MnCl_2$ + 1 ml *M* Na_3-citrate	0.02	0.0033	0.2	i 3.10 h	0.75	3.8	6
26	3	0.0005	3.5	5	1 ml *M* $Ni(NO_3)_2$ + 1 ml *M* Na_3-citrate	0.17	0.0033	0.4	i 2.98 h	0.69	0.2	5
27	3	0.0005	3.5	5	1 ml 0.01 *M* $Co(NO_3)_2$ + 1 ml *M* Na_3-citrate	12.3	0.0033	0.4	i 2.98 h	1.00	0.2	5
28	3	0.0005	3.5	5	1 ml 0.1 *M* Na_2MoO_4 + 1 ml *M* Na_3-citrate	0.86	0.0033	0.8	i 3.08 h	0.69	3.2	5
29	3	0.0005	3.5	5	1 ml 0.1 *M* $NaVO_3$ + 1 ml *M* Na_3-citrate	1.6	0.0033	0.4	i 2.95 h	0.87	1.2	5
30	3	0.0005	3.5	5	1 ml 0.01 *M* Na_2WO_4 + 1 ml *M* Na_3-citrate	4.3	0.0033	0.4	i 3.00>	0.48	0.5	8
31	3	0.0005	0.5	5	1 ml *M* $Cd(NO_3)_2$	0.07	0.0033	0.6	i 3.00 h	0.75	0.5	15
32	3	0.0005	3.5	5	1 ml 0.1 *M* $Pb(NO_3)_2$ + 1 ml *M* Na_3-citrate	0.5	0.0033	0.4	i 3.00 h	0.78	0.5	5
33	3	0.0005	3.5	5	1 ml 0.08 *M* $SbCl_3$ + 1 ml *M* Na_3-citrate	0.85	0.0033	0.4	i 2.90 h	0.78	2.8	6
34	3	0.0005	3.5	5	0.5 ml 0.2 *M* $Cu(NO_3)_2$ + 1 ml *M* Na_3-citrate	1.3	0.0033	0.4	i 3.00 h	0.88	0.5	17
35	3	0.0005	—	5	0.5 ml 0.2 *M* $Cu(NO_3)_2$ + 0.5 ml *M* H_3PO_4	1.3	0.0033	0.4	i 3.00 h	0.88	0.5	5
36	3	0.0005	3.5	5	5 ml 0.1 *M* $Th(NO_3)_4$ + 1 ml *M* Na_3-citrate	0.07	0.0033	0.6	c 2.95 h	0.69	1.2	5
37	3	0.0005	3.5	5	5 ml 0.1 *M* $Ce(NO_3)_3$ + 1 ml *M* Na_3-citrate	0.12	0.0033	0.6	i 2.95 h	0.68	1.2	5

i = intersection point; h = horizontal maximum density line; > = density increase after the end-point; c = contact point.

(Expt. 1); the minimum concentration necessary for quantitative reaction was 0.5 *M* (Expt. 1–5). The reaction with nitron always occurred instantaneously. It must therefore be assumed that this reaction is of an ionic character and that the nitron acted somehow as cation. However, it seems unlikely that 6 molecules of nitron per 1 iron atom were necessary to give the insoluble ferric-nitron-thiocyanate salt and the insoluble compound obtained may be of a more complex nature.

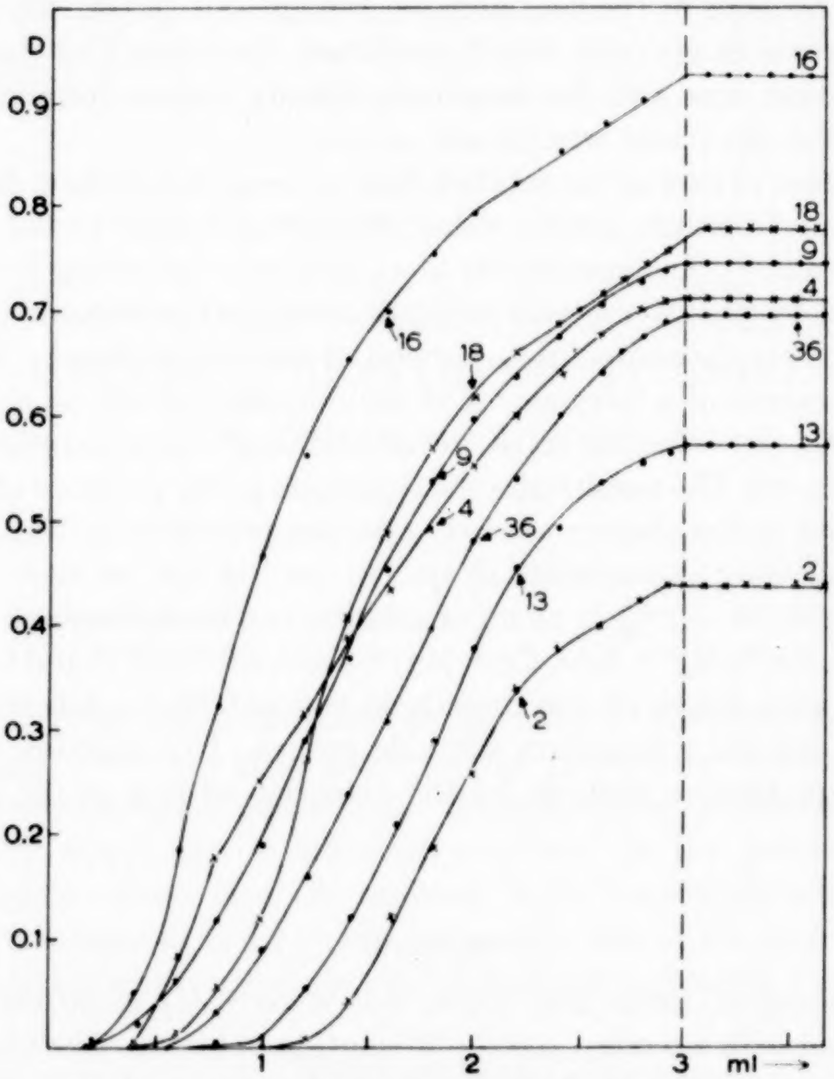

Fig. 1. Titrations of iron chloride with nitron.

Some titrations of nitron with iron chloride solutions were also carried out. The results were not so clear as in the reverse titrations, but again in most cases the above molar ratio of iron to nitron was found at the end of the titration.

When iron thiocyanate was titrated with nitron in hydrochloric acid solution, the titrant had to be added almost continuously, otherwise the density values measured soon decreased again. The same thing occurred with the maximum density values measured, which could not be stabilized. This phenomenon was apparently caused by the character of the "primary reaction" measured, and the tendency of the insoluble compound to be rearranged and redissolved. Many experiments were carried out in order to stabilize the readings of the galvanometer. When the influence of different supplements on the reaction was studied, it was found that citric acid acted very favourably in stabilizing the measurements. Therefore all further experiments

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were carried out with the addition of trisodium citrate to the hydrochloric acid solution. Some titrations were repeated with and without citric acid. In some cases, merely the presence of a foreign metal salt in concentrated solution (*e.g.* aluminium chloride, Expt. 16) was sufficient to stabilize the readings. The citric acid complexed the iron *before* it reacted with the nitron and so possibly the uncomplexed ferric iron interfered with the insoluble compound first formed. This is probably not the only reason, as the end-point density values decreased rapidly in the absence of citric acid. The favourable influence of the concentrated foreign salt (Expt. 16) may be caused partly by an increase in viscosity which weakened the activity of the primary compound. The titration time and the maximum density values obtained were usually similar whether the citric acid was present or not.

The concentration of iron in the solution had to be 0.0001–0.0002 M. Within these concentrations the maximum density values were proportional to the amount of iron present (Expt. 4 and 7). As experiments 9–11 indicate, the strong hydrochloric acid could be replaced by phosphoric acid without affecting the maximum density value or the end-point; after the end-point, a horizontal maximum density line was always obtained. The presence of a large excess of ammonium chloride or nitrate (Expt. 12 and 13) had hardly any influence on the results although the maximum density value was slightly depressed. The results of some titrations in the presence of large amounts of foreign salts but in the absence of citric acid, are presented in Expt. 15–18. From these and the following experiments (Expt. 19–25), it can be seen that less than 0.1 mg of ferric iron (*ca.* 0.1%) in 20 ml of solution can be determined in the presence of 99.9% of Ca^{+2}, Ba^{+2}, Mg^{+2}, Al^{+3}, Cr^{+3}, Mn^{+2}, Zn^{+2}, Cd^{+2}, Th^{+4} and Ce^{+3}. Thus, it is possible to determine traces of iron directly in concentrated solutions of salts of the calcium-barium and the ammonium sulphide groups. This reaction could probably also be used in qualitative analysis for the detection of iron in the presence of the above cations.

METHOD

Less than 0.1 mg of ferric iron (conc. $1–2 \times 10^{-4}$ M) in 20 ml of an aqueous solution is titrated with a 0.0025–0.0033 M solution of nitron. The test solution must contain 5 ml of 2 M KCNS, 1 ml of M citric acid and 0.5 ml of N HCl.

SUMMARY

Traces of ferric iron were determined heterometrically in concentrated solutions of potassium thiocyanate by titration with nitron. The solutions could contain 99.9% of the following cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Cr^{+3}, Al^{+3}, Mn^{+2}, Cd^{+2}, Th^{+4}, Ce^{+3} or 99% of Ni^{+2}, Pb^{+2}, Cu^{+2}, Mo^{+6}, V^{+5} and W. A titration usually lasted 5 min and in most cases the error was *ca.* 1%. The molar ratio of [Fe]:[nitron] was always equal to 1:6.6.

RÉSUMÉ

Une méthode rapide, par hétérométrie, est proposée pour le dosage de traces de fer(III). Le titrage s'effectue au moyen de nitron, dans des solutions concentrées de thiocyanate de potassium.

ZUSAMMENFASSUNG

Es wird eine ,,heterometrische" Methode beschrieben zur raschen Bestimmung von Spuren von Eisen(III) durch Titration mit Nitron in kaliumthiocyanathaltiger Lösung.

REFERENCES

[1] M. BOBTELSKY, *Anal. Chim. Acta*, 13 (1955) 172. (See literature on heterometry 1953-'56 in *Anal. Chim. Acta*, 16 (1957) 75); M. BOBTELSKY AND R. RAFAILOFF, *Anal. Chim. Acta*, 16 (1957) 321, 488; 17 (1957) 267, 308; M. BOBTELSKY AND J. EISENSTADTER, *Anal. Chim. Acta*, 16 (1957) 479; 17 (1957) 503, 579; 18 (1958) 534; 20 (1959) 216, 352; M. BOBTELSKY AND A. H. I. BEN-BASSAT, *Bull. soc. chim. France*, (1958) 180, 233, 1138; M. BOBTELSKY AND J. M. E. GOLDSCHMIDT, *Bull. Research Council Israel*, 7A (1958) 121; M. BOBTELSKY AND J. SHAMIR, *Bull. soc. chim. France*, (1958) 1569.

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GRAVIMETRIC DETERMINATION OF THORIUM AND CERIUM WITH N-BENZOYLPHENYLHYDROXYLAMINE

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N-Benzoylphenylhydroxylamine was recommended for the precipitation and determination of metals[1,2] and has been used[3] for the gravimetric estimation of molybdenum. SHOME[1] observed that the reagent forms insoluble complexes with thorium, cerium and other metal ions in aqueous solutions. In the present investigation thorium and cerium have been determined with benzoylphenylhydroxylamine; thorium has been separated from cerium by making use of the fact that thorium is precipitated at pH 5.0 whilst cerous ion is precipitated at pH 7.0.

EXPERIMENTAL

Solutions of metals

Standard solutions of thorium nitrate and ceric ammonium nitrate were prepared to contain respectively 2.84 mg of thorium dioxide and 2.408 mg of cerium dioxide per ml.

All the chemicals employed were of A.R. quality.

DETERMINATION OF THORIUM

A known amount of the thorium nitrate solution (25 to 30 ml) was diluted with distilled water to 250 ml, and 10% ammonium acetate solution was added to adjust the pH to about 5.0; the pH value was ascertained with indicator paper. Benzoylphenylhydroxylamine (0.3 to 0.4 g) in alcohol (10 to 15 ml) was then added with constant stirring. The white precipitate was occasionally stirred for 15 min, filtered, washed with water, ignited to dioxide in a porcelain crucible and weighed.

The results (Table I) show that thorium is precipitated quantitatively with benzoylphenylhydroxylamine between pH 4.5 and 5.5 and the metal can be determined by igniting the precipitate to thorium dioxide and weighing.

TABLE I

DETERMINATION OF THORIUM WITH BENZOYLPHENYLHYDROXYLAMINE

Thorium dioxide		*Error*
taken (g)	*found(g)*	*g*
0.0710	0.0705	— 0.0005
0.0738	0.0733	— 0.0005
0.0767	0.0761	— 0.0006
0.0794	0.0790	— 0.0004
0.0852	0.0846	— 0.0006

pH of solutions = 4.5 to 5.5

DETERMINATION OF CERIUM

A known quantity of the ceric ammonium nitrate solution (25 to 30 ml) was heated to boiling and 5% hydroxylamine hydrochloride solution (10 ml) was added to reduce the ceric ions. The solution was diluted to 250 ml, allowed to cool and 10 ml of the hydroxylamine hydrochloride solution was added to prevent oxidation of the cerous ions during the subsequent precipitation. Benzoylphenylhydroxylamine (0.3 to 0.4 g) in alcohol (10 to 15 ml) was then added and the pH of the solution was raised to about 7.0 by adding 1*N* ammonium hydroxide solution to complete the precipitation. The white precipitate was occasionally stirred for 30 min, filtered, washed, ignited to cerium dioxide and weighed.

TABLE II

DETERMINATION OF CERIUM WITH BENZOYLPHENYLHYDROXYLAMINE

Cerium dioxide		*Error*
taken(g)	*found(g)*	*g*
0.0602	0.0596	— 0.0006
0.0626	0.0629	+ 0.0003
0.0650	0.0649	— 0.0001
0.0674	0.0678	+ 0.0004
0.0722	0.0719	— 0.0003

pH of solutions = 6.5 to 7.5

The precipitation of trivalent cerium (Table II) with benzoylphenylhydroxylamine was complete between pH 6.5 and 7.5; above pH 7.5 the reagent solution gradually assumed a red colour. The ceric ions could be precipitated with benzoylphenylhydroxylamine at pH. 5.0, but the ceric complex was difficult to filter because of its gelatinous nature.

SEPARATION OF THORIUM AND CERIUM

A mixture containing known amounts of the thorium and ceric solutions was heated to boiling and hydroxylamine hydrochloride solution was added as above. The solution was cooled, diluted to 250 ml and more hydroxylamine hydrochloride solution (10 ml) was added. The pH of the solution was then raised to about 5.0 and thorium precipitated as described above. The precipitate was filtered and immediately washed with a freshly prepared 0.1% hydroxylamine hydrochloride solution and finally with distilled water. The precipitate was dried and ignited to thorium dioxide. The filtrate and washings were evaporated to about 250 ml and hydroxylamine hydrochloride solution (10 ml) was added to prevent the formation of any ceric complex. The cerous ion was then determined as described above.

The results (Table III) show that thorium can be separated from cerium and the individual metals determined by means of benzoylphenylhydroxylamine. During the concentration of the combined filtrate and washings, solid organic matter appeared, which was probably formed by the prolonged heating of the reagent solution in air.

TABLE III

SEPARATION OF THORIUM AND CERIUM WITH BENZOYLPHENYLHYDROXYLAMINE

Mixture No.	*Thorium dioxide*		*Cerium dioxide*	
	taken g	*found* g	*taken* g	*found* g
1	0.0852	0.0849	0.0602	0.0598
2	0.0909	0.0907	0.0626	0.0628
3	0.0794	0.0787	0.0650	0.0652
4	0.0767	0.0768	0.0722	0.0717
5	0.0625	0.0629	0.0938	0.0941

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One of us (S. K. S.) is indebted to the Ministry of Scientific Research and Cultural Affairs, Government of India, for the award of a scholarship.

SUMMARY

Benzoylphenylhydroxylamine has been used for the precipitation of thorium and trivalent cerium; the precipitates are ignited to the corresponding metal dioxide and weighed. Ceric ions are reduced before precipitation. The gravimetric separation of thorium and cerium is effected by precipitation at different pH values.

RÉSUMÉ

La benzoylphénylhydroxylamine est proposée comme réactif pour le dosage gravimétrique du thorium et du cérium. Il est possible de séparer ces deux éléments en effectuant la précipitation à des pH différents.

ZUSAMMENFASSUNG

Zur gravimetrischen Bestimmung von Thorium und Cer kann Benzoylphenylhydroxylamin verwendet werden. Bei Einhaltung bestimmter pH-Werte lassen sich die beiden Metalle getrennt fällen.

REFERENCES

[1] S. C. Shome, *Current Sci. India*, 13 (1944) 257.
[2] S. C. Shome, *Analyst*, 75 (1950) 27; *Anal. Chem.*, 23 (1951) 1186.
[3] S. K. Sinha and S. C. Shome, *Current Sci. India*, 26 (1957) 249.

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A SPECIFIC METHOD FOR THE DETERMINATION OF URANIUM IN ORES BY CATHODE RAY POLAROGRAPHY

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INTRODUCTION

In recent years polarographic procedures have been extensively applied to the determination of uranium in ores. Among the many base electrolytes employed may be mentioned the acid-tartrate method of LEWIS AND OVERTON[1,2], the acid-oxalate method of LEGGE[3], and the ascorbic acid method of SUSIC[4]. While some doubt appears to exist regarding the selectivity of these base electrolytes towards uranium[5], the acid–tartrate and the ascorbic acid base electrolytes appear to be the most selective of those available. A systematic study of interferences in these two methods indicated, however, that they may not, in general, be directly applied to the determination of uranium in ores. Considering the low concentrations of uranium frequently present in these ores, and the wide variety of foreign elements associated with uranium, it is usually necessary to separate the uranium from the bulk of the impurities. Vanadium, in particular, interferes seriously in most polarographic determinations of uranium[6,7], and is also difficult to completely separate from uranium prior to the determination[8].

The methods most commonly used for the purification of the uranium solution are chromatography[9], solvent extraction[10], and ion-exchange[11]. Chromatography and solvent extraction suffer from the disadvantage that large amounts of organic solvents are employed which must be completely removed before the polarographic determination. The anion-exchange separation of uranium on a strongly-basic resin from dilute sulphate solutions[11] is apparently the most selective available, but difficulty was experienced in this laboratory in obtaining complete recovery and good separation of the uranium at the same time. A mercury cathode separation of uranium appears ideal where a polarographic finish to the determination is contemplated, since a large number of foreign elements are removed, the operation is simple and rapid, and the solution comes in contact only with glass, mercury and platinum. In this paper a procedure is described, using a small mercury cathode cell, which allows the uranium to be separated in less than one hour by the "constant current" electrolysis technique. A base electrolyte has been developed in which elements not removed by the mercury cathode electrolysis, do not interfere in the polarographic determination of uranium. This base electrolyte is considered the most selective yet developed for uranium, and combined with a previous mercury cathode separation, the method appears specific for uranium in ores processed in this country.

APPARATUS

A linear-sweep cathode ray polarograph equipped with an electrode stand and constant temperature water bath, from Southern Instruments Computer Division, Surrey, England, was used for the experimental work. This instrument is of the DAVIS type[12], with a voltage sweep rate of 0.3 V per sec, a sweep time of 2 sec and a delay period of 5 sec. A polarographic cell employing a mercury pool anode was used throughout. All polarographic measurements were made at 25°.

Mercury cathode electrolysis cell

This cell is illustrated in Fig. 1. An aliquot of the solution may be withdrawn from the cell without interrupting the electrolysis by means of a pipette inserted through the air-condenser socket. The surface of the mercury may be stirred with a magnetic stirrer, or alternatively, by vibration.

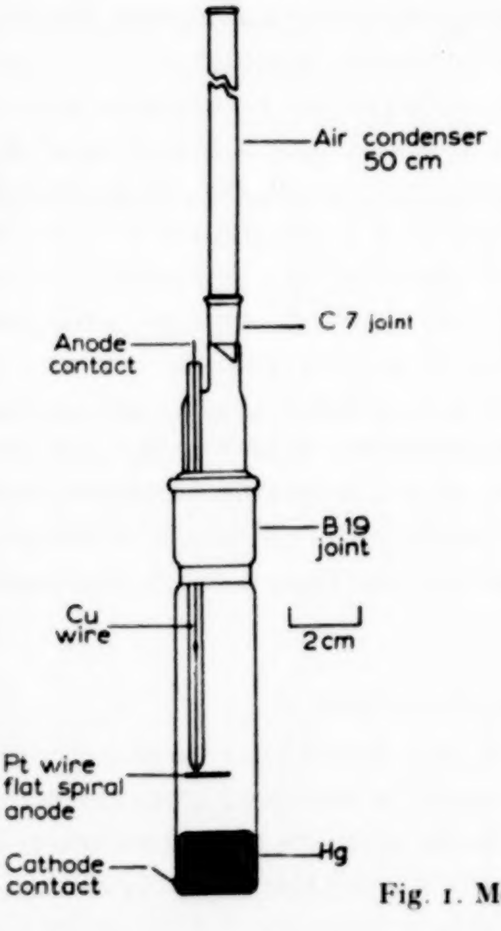

Fig. 1. Mercury cathode cell.

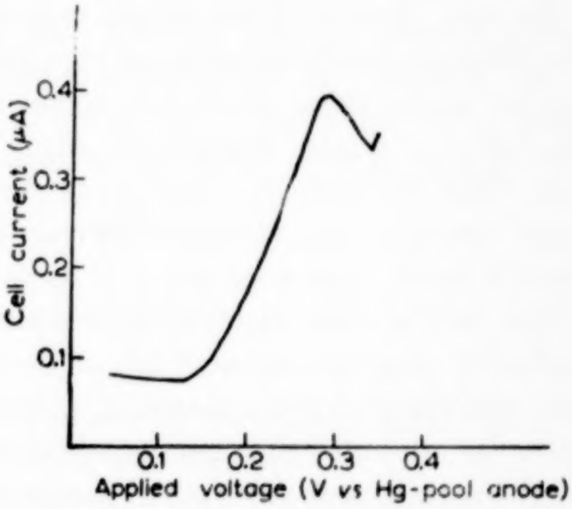

Fig. 2. Polarography of $2 \cdot 10^{-5}$ *M* uranium in "mixed" base electrolyte.

REAGENTS

Base electrolyte stock solution

Dissolve the following reagents in demineralized water, and dilute to 1 l: tribasic ammonium citrate (194 g), citric acid monohydrate (84 g), ammonium oxalate monohydrate (14.2 g), disodium ethylene diamine tetraacetate dihydrate (37 g), sodium chloride (5.85 g). The chemicals used should be the purest grade available.

This stock solution was purified by a controlled-potential mercury cathode electrolysis, using a cell of 1.5-l capacity[13], a cylindrical platinum-gauze anode, and a silver–silver chloride reference electrode. The potential of the mercury cathode was maintained by a manually operated circuit at —0.8 V *versus* the reference electrode for 5 h. The purified solution was filtered into a polythene storage bottle.

The pH of this solution should be 4.7 at 25°.

1.0 M ascorbic acid

High purity *l*-ascorbic acid from C.S.R. Chemicals Pty. Ltd., Sydney, was used for the preparation of this solution. Dissolve 17.6 g of ascorbic acid in water and dilute to 100 ml. This solution should be prepared fresh daily.

All other chemicals used were of A.R. quality.

PROCEDURE FOR THE DETERMINATION OF URANIUM IN ORES

Weigh a suitable amount of the very finely ground ore directly into a small platinum dish. Add 5 ml of conc. HNO_3 and 5 ml of 50% H_2F_2. Swirl gently, and evaporate the solution just to dryness. Add further 5-ml portions of HNO_3 and H_2F_2 and repeat the evaporation until solution of the ore is complete. Add sufficient 72% $HClO_4$ to make the sample solution, when diluted to volume, 0.1 *N* in $HClO_4$. Heat to fumes of $HClO_4$ for a few min, then cool and dilute to volume with water in a volumetric flask. The sample solution should be between 10^{-5} and $2 \cdot 10^{-4}$ molar in uranium.

Transfer about 15 ml of solution to the mercury cathode cell. Electrolyse at 6 – 9 V (1.5 A) for 40 – 60 min. Remove the air condenser and withdraw a 5-ml aliquot of the solution while electrolysis is still proceeding. Transfer to a small, dry, stoppered flask and cool under a tap to room temperature. Pipette a 2-ml aliquot into a 10-ml volumetric flask. Add 2 ml of 1.0 *M* ascorbic acid, one drop of 5 *N* NaOH, and mix. Add 5 ml of the base electrolyte stock solution and dilute to volume with water. Immediately transfer about 3 ml of this solution to a polarographic cell and pass nitrogen gas through the solution at a slow rate for 5 – 10 min. Using a start potential of zero volts, measure the peak current occurring at about —0.28 V *v.* Hg pool anode. Under the same conditions record the peak current due to a standard uranyl perchlorate solution of approximately the same concentration as the unknown. After correction of the results for residual current, which should be less than 0.01 μA, the uranium content of the ore may be calculated.

THE MERCURY CATHODE SEPARATION

Using the cell, and the procedure described, it was found that large amounts of copper, iron, molybdenum, tin and other metals could be removed from the solution in less than 30 min. It is interesting to note that if the uranium concentration is kept below $5 \cdot 10^{-4} M$ no net reduction of uranium occurs during the electrolysis in 0.1 *N* $HClO_4$. This phenomenon does not occur with dilute uranium solutions in 0.1 *N* H_2SO_4 nor with more concentrated uranium solutions in 0.1 *N* $HClO_4$. Here considerable reduction occurs during electrolysis, and the solution must be reoxidized before the polarographic determination is carried out. It is believed the presence of a small amount of oxidizing agent, *e.g.* chlorine formed by the decomposition of some perchloric acid, is sufficient to reoxidize the dilute uranium solution.

COMPOSITION OF THE BASE ELECTROLYTE

Of the elements which remain in solution with uranium after a mercury cathode electrolysis, vanadium, titanium and tungsten are most likely to interfere in the subsequent polarographic determination of uranium. The interference of vanadium has been shown[6] to be partly due to oxidation of pentavalent uranium by tetravalent vanadium:

$$UO_2^{+} + VO^{+2} + 2H^{+} = UO_2^{+2} + V^{+3} + H_2O$$

The regenerated uranyl ions are then available for further reduction, leading to erroneously high diffusion currents. Since considerable amounts of vanadium are commonly encountered in uranium ores, this interference is serious. Many previously published base electrolytes for uranium were investigated, but none could tolerate even moderate amounts of vanadium.

It is known[14,15], that vanadium, particularly VO^{+2} and V^{+3}, forms strong complexes with ethylenediaminetetraacetic acid (EDTA). In a base electrolyte consisting of ascorbic acid and EDTA no reduction wave for vanadium is evident, and vanadium up to 200 times the uranium concentration may be present before interference occurs. This base electrolyte is quite selective towards uranium, but unfortunately even small amounts of titanium interfere. By adding citric acid and maintaining the pH at 4 – 5, the titanium reduction wave is shifted to a very negative potential, and an ascorbate–EDTA–citrate base electrolyte will tolerate large concentrations of titanium. In this medium, however, a double uranium wave is obtained, the first wave representing the reduction of the uranyl ion to the pentavalent state, and the second wave, occurring at a slightly more negative potential, is probably due to disproportionation of the pentavalent uranium:

$$UO_2^{+2} + e = UO_2^{+} \qquad (1)$$

then

$$2\,UO_2^{+} + H^{+} = UO_2^{+2} + UO(OH)^{+} \qquad (2)$$

TABLE I

INTERFERENCE OF DIVERSE CATIONS IN THE ASCORBATE, TARTRATE AND "MIXED" BASE ELECTROLYTES FOR THE DETERMINATION OF URANIUM

Showing the concentration level, 100 : 1, 10 : 1, 1 : 1 or 0.1 : 1 corresponding to foreign element : uranium, at which interference first occurs. Uranium conc. in all cases $8 \cdot 10^{-4}$%

Ion	*Ascorbate*	*Tartrate*	*"Mixed"*
Al^{+3}	nil	nil	nil[b]
As^{+3}	nil	nil	nil
Bi^{+3}	1 : 1	10 : 1	nil
Ca^{+2}	nil	nil	nil
Cd^{+2}	nil	nil	nil
Ce^{+4}	nil	nil	nil
Co^{+2}	nil	nil	nil
Cr^{+6}	nil	1 : 1	10 : 1
Cu^{+2}	1 : 1	0.1 : 1	0.1 : 1
Fe^{+3}	nil	10 : 1[a]	10 : 1
Mg^{+2}	nil	nil	nil
Mn^{+2}	nil	nil	nil
Mo^{+6}	0.1 : 1	0.1 : 1	1 : 1
Ni^{+2}	nil	nil	nil
Pb^{+2}	0.1 : 1	nil	nil
Sb^{+3}	100 : 1	100 : 1	nil
Sn^{+2}	0.1 : 1	0.1 : 1	10 : 1[a]
Te^{+6}	0.1 : 1	nil	nil
Th^{+4}	nil	nil	nil
Ti^{+4}	100 : 1	1 : 1	nil
Tl^{+}	10 : 1	100 : 1	1 : 1
V^{+5}	1 : 1	0.1 : 1	nil
W^{+6}	0.1 : 1	1 : 1	100 : 1
Zn^{+2}	nil	nil	nil
Zr^{+4}	nil	nil	nil

[a] **peak potential altered;** [b] **double wave obtained.**

By adding a small amount of ammonium oxalate, a single uranium wave is again obtained, its height being equal to the sum of the two previous waves. The oxalate ion forms strong complexes with both hexavalent and tetravalent uranium[16], and apparently accelerates reaction (2).

The final composition of the base electrolyte is then: 0.2 *M* ascorbic acid, 0.4 *M* ammonium citrate, 0.2 *M* citric acid, 0.05 *M* ammonium oxalate, 0.05 *M* EDTA and 0.05 *M* sodium chloride. The sodium chloride is added to enable a mercury-pool anode to be used.

While this base electrolyte is admittedly complex, this is no disadvantage, as the constituents, with the exception of ascorbic acid, are stable and compatible, and a concentrated stock solution may be prepared and stored indefinitely. Small variations in the composition of the base electrolyte do not affect the determination. If the uranium concentration is below 10^{-4} *M*, a particularly well formed wave is obtained with a very flat base line (Fig. 2). With larger amounts of uranium the wave becomes drawn out and ill defined.

STUDY OF INTERFERENCES

Table I shows the effect of diverse ions in the ascorbate, acid–tartrate, and the citrate–oxalate – EDTA – ascorbate ("mixed") base electrolytes for the determination of uranium using a Cathode Ray polarograph and a Hg-pool anode.

The 1 *M* H_2SO_4, 0.05 *M* sodium tartrate base was prepared as directed by SHALGOSKY[2] (no maximum suppressor), and the ascorbate base was 0.5 *M* ascorbic acid containing 0.05 *M* sodium chloride and adjusted to pH 3.7. The final solutions contained $8 \cdot 10^{-4}\%$ uranium, and $8 \cdot 10^{-2}\%$, $8 \cdot 10^{-3}\%$, $8 \cdot 10^{-4}\%$, and $8 \cdot 10^{-5}\%$ respectively of the particular element for the concentration levels 100 : 1, 10 : 1, 1 : 1 and 0.1 : 1 element to uranium. The table shows the concentration level at which interference (2% error in peak current) first occurs.

Whenever possible the foreign elements were added as the perchlorates, prepared by solution of the element or its oxide in perchloric acid.

It may be seen from the table that Bi^{+3}, Cr^{+6}, Cu^{+2}, Fe^{+3}, Mo^{+6}, Sn^{+2}, Ti^{+4}, V^{+5} and W^{+6} interfere seriously in the acid–tartrate method. Using the ascorbate base electrolyte at pH 3.7, Bi^{+3}, Cu^{+2}, Mo^{+6}, Pb^{+2}, Sn^{+2}, Te^{+6}, Tl^{+}, V^{+5} and W^{+6} interfere seriously. With the "mixed" base Cr^{+6}, Cu^{+2}, Fe^{+3}, Mo^{+6}, Sn^{+2} and Tl^{+} interfere. Tungsten does not interfere if it is less than 50 times the uranium concentration. If more than 5 mg of aluminium is present in the final solution a double wave is obtained, presumably due to the removal of oxalate ions by Al^{+3}. While iron is reduced completely by ascorbic acid, on the addition of the base electrolyte a ferric wave gradually reappears. This is probably due to the formation and oxidation of a ferrous–EDTA complex, which is known to be very rapidly oxidized by air[17].

In addition to the cations shown, the "mixed" base electrolyte was found to be unaffected by large amounts of sulphate, chloride, nitrate and phosphate.

COMPARISON OF BASE ELECTROLYTES

Table II compares the peak potentials and sensitivities of the acid–tartrate, ascorbate and "mixed" base electrolytes at a uranium concentration of $2 \cdot 10^{-5}$ *M*.

It is seen that at the uranium concentration used, the "mixed" base electrolyte is somewhat more sensitive than the other two.

TABLE II

COMPARISON OF PEAK POTENTIALS AND SENSITIVITIES OF THE TARTRATE, ASCORBATE AND "MIXED" BASE ELECTROLYTES FOR THE DETERMINATION OF URANIUM

Base electrolyte	*Peak potential in V versus Hg-pool anode (0.05 M chloride)*	*$K = ip/C$ µA/mmoles/l[a] for a UO_2^{+2} concn. of $2 \cdot 10^{-5}$ moles/l*
Tartrate	—0.38	13.4
Ascorbate	—0.27	13.0
"Mixed"	—0.28	14.1

[a] ip = peak current for $m = 1.14$ mg/sec $t = 6.5$ sec

RELATIONSHIP BETWEEN URANIUM CONCENTRATION AND PEAK CURRENT

It may be seen from Table III that peak current is proportional to concentration in the "mixed" base electrolyte if the uranium concentration is below $4 \cdot 10^{-5}$ *M*. Above this value the peak current becomes proportionally less, the reduction wave gradually assumes an irreversible nature, and the peak potential shifts to more negative values.

TABLE III

RELATIONSHIP OF PEAK CURRENT TO CONCENTRATION OF URANYL ION IN THE "MIXED" BASE ELECTROLYTE AT 25°

UO_2^{+2} concn. (C) moles/l	*Peak current ip µA*	*$K = ip/C$ µA/mmoles/l*
$1 \cdot 10^{-3}$	9.80	9.80
$5 \cdot 10^{-4}$	5.11	10.3
$2 \cdot 10^{-4}$	2.22	11.1
$1 \cdot 10^{-4}$	1.21	12.1
$5 \cdot 10^{-5}$	0.658	13.2
$4 \cdot 10^{-5}$	0.559	14.0
$2 \cdot 10^{-5}$	0.282	14.1
$1 \cdot 10^{-5}$	0.142	14.2
$5 \cdot 10^{-6}$	0.0705	14.1
$2 \cdot 10^{-6}$	0.0280	14.0
$1 \cdot 10^{-6}$	0.0141	14.1
$5 \cdot 10^{-7}$	0.0070	14.0

ANALYSIS OF ORES

Table IV shows the results obtained on ten samples of uranium ores by the polarographic method described above. The results on ores No. 1 – 7 are compared with those obtained by an independent research organisation using the classical method consisting of a cellulose column separation of the uranium from nitric acid–ether solution, followed by spectrophotometric determination with hydrogen peroxide. Ores No. 8 – 10 were analysed fluorometrically by an independent laboratory.

In addition to uranium, ores No. 1 – 7 were found to contain silica (25 – 85%),

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iron (5 – 65%), vanadium (0.2 – 2.0%), copper (0.05 – 0.2%), and small amounts of the following elements: Al, Pb, Cr, Ti, Mo, Ni, Ag, Au, Bi, W and Mn.

To test the precision of the procedure outlined, ten portions of ore No. 5 were carefully analysed. The results gave a standard deviation ($n-1$) of 1.9%.

TABLE IV

APPLICATION OF THE "MIXED" BASE ELECTROLYTE POLAROGRAPHIC METHOD FOR URANIUM TO THE DETERMINATION OF URANIUM IN ORES

Ore No.	*Reference method % U_3O_8*	*"mixed base" polarographic method % U_3O_8*	*Difference %*
1	8.3	8.3	—
2	7.6	7.5	—1.3
3	0.72	0.73	+1.4
4	0.65	0.65	—
5	0.55	0.55	—
6	0.42	0.44	+4.8
7	0.34	0.35	+2.9
8	0.037	0.046	+24
9	0.020	0.025	+25
10	0.011	0.014	+27

SUMMARY

A method is presented for the specific determination of uranium in ores by cathode ray polarography. The uranium is separated by a simple and rapid mercury-cathode electrolysis, then determined polarographically in a base electrolyte in which vanadium, titanium and tungsten do not interfere. Application of the method to the analysis of ten standard uranium ores is shown.

RÉSUMÉ

Une méthode spécifique, par polarographie à rayons cathodiques, est proposée pour le dosage de l'uranium dans ses minerais. L'uranium est préalablement séparé par électrolyse sur cathode de mercure.

ZUSAMMENFASSUNG

Es wird eine spezifische Methode beschrieben zur Bestimmung von Uran in Erzen durch Kathodenstrahlen-Polarographie nach elektrolytischer Abtrennung mit einer Quecksilberkathode.

REFERENCES

[1] J. A. Lewis and K. C. Overton, Department of Scientific and Industrial Research, Chemical Research Laboratory; *Scientific Report C R L/ A E.*, 41 (1949).

[2] H. I. Shalgosky, *Analyst*, 81 (1956) 512.

[3] D. I. Legge, *Anal. Chem.*, 26 (1954) 1617.

[4] M. V. Susic, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, Session 15 B.2, P/964, 1955.

[5] T. W. Steele and L. Taverner, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy*, A/Conf. 15 P/1117, 1958.

[6] Yu. V. Morachevsky and A. A. Sakharov, *Zhur. Anal. Khim.*, 13 (1958) 83, 457.

[7] M. A. De Sesa, *U.S.A.E.C. Report T I D* – 7555.

[8] Yu. V. Morachevsky and A. A. Sakharov, *Zhur. Anal. Khim.*, 13 (1958) 575.

[9] F. H. Burstall and R. A. Wells, *Analyst*, 76 (1951) 396.

[10] O. A. Nietzel and M. A. De Sesa, *Anal. Chem.*, 29 (1957) 756.

[11] S. Fisher and R. Kunin, *Anal. Chem.*, 29 (1957) 400.

[12] H. M. Davis, *British Patent No. 702685.*

[13] J. J. Lingane, *Electroanalytical Chemistry*, Interscience Publishers, Inc., New York 1953, p.324.

[14] G. Schwarzenbach and J. Sandera, *Helv. Chim. Acta*, 36 (1953) 1089.

[15] R. L. Pecsok and R. S. Juvet, *J. Am. Chem. Soc.*, 75 (1953) 1202.

[16] C. J. Rodden, "*Analytical Chemistry of the Manhattan Project*", McGraw-Hill Book Company, Inc., New York 1950, p.13.

[17] I. M. Kolthoff and C. Auerbach, *J. Am. Chem. Soc.*, 74 (1952) 1452.

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THE POLAROGRAPHIC DETERMINATION OF CHROMIUM IN ALUMINUM ALLOYS

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INTRODUCTION

The determination of chromium in aluminum alloys is based mainly on titrimetric or photometric methods. The only polarographic method found in the literature[1] entails a rather elaborate preparation of the sample; after dissolution of the sample in an acid mixture, it is twice evaporated to sulphuric acid fumes, and, in alloys containing more than 0.25% copper, copper is removed by prior electrolysis.

The development of a convenient polarographic method for the determination of chromium in aluminum alloys appeared desirable. The method proposed is based on dissolution of the alloy in a bromine water–sodium hydroxide mixture; subsequent filtration affords a simple separation of the hexavalent chromium from all the constituents of the alloy except those soluble in sodium hydroxide. Excess hypobromite is easily removed by the addition of ammonia solution to the filtered sample solution[2], which may then be made up to volume and used directly for the polarographic determination of chromium.

The reduction of hexavalent to trivalent chromium in 1 *N* sodium hydroxide solution affords a well-developed polarographic wave[3], which lends itself admirably to quantitative interpretation. Aluminum, titanium and zinc, the only constituents of the alloy accompanying the chromium in the filtered solution, do not interfere with this wave.

EXPERIMENTAL

Apparatus

A Type E. Leeds Northrup Electro-Chemograph (pen recording polarograph) was used. Damping "2" was employed throughout.

Since the medium chosen for recording the polarograms was strongly alkaline, attacking the capillaries and making their frequent replacement necessary, methods of quantitative interpretation independent of the capillary characteristics were employed. The drop time, the amount of mercury flowing through the capillary and the height of the mercury column are, therefore, not reported. All samples were thermostatted at 25° ± 0.1° and de-aerated with purified nitrogen before the polarograms were recorded. 100-ml Pyrex glass beakers were used as polarographic cells, with a Lingane type[4] S.C.E. serving as reference electrode.

Standard solutions and reagents

1. Standard potassium dichromate solution (prepared by dissolving 0.2829 g of dried potassium dichromate in water and making up to 1 l. This solution contains 0.1 mg Cr per ml). 2. Bromine water, saturated. 3. Sodium hydroxide solution, conc. (prepared daily, by dissolving 30 g of sodium hydroxide in 50 ml of water). 4. Sodium hydroxide solution, 3%. 5. Ammonia solution (1 : 1). 6. Triton X-100 solution, 0.2%. (This is a non-ionic detergent, manufactured by Rohm and Haas Co., which served as maximum suppressor.) 7. British Chemical Standards Alloy, No. 263. This is a magnesium–aluminum alloy, containing 0.34% Cr, and also Cu, Mg, Si, Fe, Mn, Zn and Ti. 8. Aluminum metal, pure.

All reagents employed were of analytical quality.

PROCEDURE

Preparation of the sample solution

0.250–0.500 g of the alloy, containing about 1 mg of chromium was weighed into a 100-ml Pyrex glass beaker; 10 ml of the saturated bromine water were added, followed by 5 ml of the conc. sodium hydroxide solution. After the initial effervescence had subsided, the mixture was heated gently to effect complete dissolution of the alloy and then boiled for 5 min. An additional portion of 5 ml of bromine water was added and the mixture boiled again. After cooling, 5 ml of the ammonia solution were added with continuous stirring, and the mixture was set aside for 5 min, heated gently and filtered into a 100-ml volumetric flask. The beaker, filter paper and precipitate were thoroughly washed with warm 3% sodium hydroxide solution. After cooling, 0.5 ml of the Triton X-100 solution was added and the solution was made up to volume with 3% sodium hydroxide solution.

Preparation of the blank solution

A second portion of the alloy, equal in weight to that taken for the preparation of the sample solution, was weighed into a 100-ml Pyrex glass beaker, 10 ml of distilled water and 5 ml of the sodium hydroxide solution were added, and after dissolution of the alloy, the mixture was boiled for 5 min and filtered into a second 100-ml Pyrex glass beaker. 15 ml of the saturated bromine water and 5 ml of the ammonium hydroxide solution were mixed in a third beaker and set aside for 5 min to ensure complete destruction of bromine. This mixture was added to the alloy filtrate, the solution heated (some iron may precipitate at this stage) and filtered into a 100-ml volumetric flask. After the addition of 0.5 ml of Triton X-100 solution, the solution was made up to volume with 3% sodium hydroxide solution.

Recording of the polarograms and their quantitative interpretation

The polarograms of the following solutions must be recorded:

1. the blank solution,
2. 50 ml of the sample solution pipetted into a dry, 100-ml beaker, and
3. the above solution (2), after the addition of 5 ml of the standard potassium dichromate solution.

Experimental conditions during recording must be kept constant, *i.e.* the same capillary, height of mercury column and galvanometer sensitivity must be employed for all three polarograms.

Temperature constancy must be ensured by the use of a suitable thermostat and oxygen removed by thorough de-aeration. The polarograms were recorded from —0.3 V to — 1.3 V *vs.* S.C.E. Diffusion currents were measured by drawing a line connecting the peaks of the polarogram at —0.55 V and —0.70 V *vs.* S.C.E. and extrapolating it to —1.25 V *vs.* S.C.E.; the distance from this point to the peak of the polarogram at the same potential was taken to represent the diffusion current. The chromium content of the alloy was calculated from the following formula:

$$\%\text{Cr} = \frac{(i_2 - i_1)}{(11(i_3 - i_1) - 10(i_2 - i_1))w}$$

where i_1, i_2 and i_3 are the diffusion currents obtained by the above method from polarograms of solutions 1, 2 and 3 respectively, and w is the weight of alloy in grams taken for the preparation of the sample and blank solutions.

DISCUSSION

Preparation of the sample solution

1. The dissolution of aluminum alloys in conc. sodium hydroxide solution is very convenient; in this medium, the choice of oxidizing agents available for the quantitative oxidation of chromium to the hexavalent state is rather restricted[5-8]. An alkaline bromine mixture was finally chosen because it ensured the formation of chromium(VI) from the outset, thus preventing the retention of chromium(III) in the hydroxide precipitate. Excess oxidizing agent must be removed quantitatively before the polarography; in the case of bromine, this was easily achieved by the addition of ammonia solution. The precipitate contains the hydroxides or oxides of iron, copper, manganese, nickel, etc.; chromium, zinc, aluminum and titanium pass into the filtrate. In the case of alloys containing lead, this also remains in the precipitate, because metallic lead does not dissolve in the medium used.

2. The accuracy of the results obtained by this method depends on the meticulous preparation of the blank solution containing the alloy and all the reagents used in the preparation of the sample solution, and differing from it only in the oxidation state of the chromium. Common reagent solutions must therefore be employed for the preparation of both sample and blank solutions and the volumes indicated in the procedure must be measured carefully.

3. The reagents must be introduced in the exact order given in the procedure to prevent the precipitation of chromic hydroxide; for that reason, bromine water must be added before the sodium hydroxide solution. The second portion of bromine water ensures the quantitative oxidation of the chromium.

4. Alloy samples containing considerable amounts of copper must be prepared by a slightly different method, owing to the appreciable solubility of cupric oxide in ammonia solution.

A preliminary filtration step, immediately after dissolution of the sample and before the addition of ammonia solution, prevents the passage of copper into the final sample solution. This filtration does not replace the filtration indicated in the procedure, which serves to remove traces of precipitate formed at this stage.

Preparation of the blank solution

1. The procedure recommended for the preparation of the blank solution ensures its similarity to the sample solution in all respects except the oxidation state of the chromium. Distilled water replaces the initial bromine water, and a mixture of the appropriate volumes of bromine water and ammonia solution is added to the filtrate (this mixture must be previously prepared in a separate beaker, so that all the bromine is destroyed before its addition to the blank solution).

The polarographic determination

The reduction of chromate ion in sodium hydroxide medium (0.1 – 1.0 N) gives rise to a well-defined polarographic wave, whose half-wave potential is —0.85 V *vs.* S.C.E. The diffusion current is proportional to the concentration of chromate[3]. The residual current cannot be deducted by the usual method of extrapolating the part of the polarographic curve preceding the wave to the potential at which it is desired to measure the diffusion current, because a polarogram of the supporting electrolyte alone also shows a small but distinct polarographic wave in this region. The diffusion current of this wave, which results mainly from the reduction of traces of iron present in the alkaline solution[9], must be deducted from the diffusion current observed with chromate solutions. In the analysis of alloy samples, this blank diffusion current may be a considerable part of the measured chromate reduction diffusion current, and its exact determination is essential; hence, the sample solution and blank solution are prepared so that all factors, such as alkalinity, ionic strength, etc., are kept equal in both. Provided that this condition is fulfilled, the deduction of the blank diffusion current from that of the sample solution gives a diffusion current proportional to the chromium content of the sample.

2. The standard addition method was chosen as most appropriate for this determination, because the strongly alkaline medium in which the polarograms must be recorded necessitates the frequent replacement of capillaries, and because standard potassium dichromate solutions are easily prepared and stored.

TABLE I

Alloy No.	*Weight of sample (w) g*	i_1 *mm**	i_2 *mm*	i_3 *mm*	*Chromium*	
					theor. %	*found* %
1	0.500	48	75	101	0.17	0.17
1	0.500	48	73	99	0.17	0.16
2	0.250	18.5	47.5	85.5	0.25	0.26
2	0.250	18.5	44.5	80.5	0.25	0.25
3	0.250	16	58	86	0.50	0.48
3	0.250	19	63	91.5	0.50	0.50
4	0.250	17.5	50	81	0.34	0.35
4	0.250	17.5	50	82	0.34	0.34

* The diffusion currents i_1, i_2 and i_3 are reported, as measured in the course of the analysis, in mm, there being no need of converting them into μA (only current ratios are involved in the calculation of results).

RESULTS

The procedure was tested with aluminum alloys containing 0.1–0.5% chromium; various proportions of British Chemical Standards Alloy, No. 263, pure aluminum metal and standard potassium dichromate solution were mixed, and the synthetic alloys thus obtained were analyzed.

Table I shows some of the results obtained.

SUMMARY

A convenient polarographic method for the determination of 0.1–0.5% of chromium in aluminum alloys is described. The alloy is dissolved in a bromine water–sodium hydroxide mixture; after suitable treatment, chromate is determined polarographically. Specific directions for the simultaneous running of a blank experiment are given; this provision greatly improves the accuracy of the results obtained.

RÉSUMÉ

Une méthode polarographique est proposée pour le dosage du chrome (0.1 à 0.5%) dans les alliages à base d'aluminium. Le chrome se trouve sous forme de chromate, après attaque de l'échantillon à analyser par l'eau de brome et l'hydroxyde de sodium.

ZUSAMMENFASSUNG

Es wird eine polarographische Methode zur Bestimmung von Chrom (0.1–0.5%) in Aluminiumlegierungen beschrieben. Die Legierung wird in einem Gemisch von Natriumhydroxyd und Bromwasser gelöst und das entstandene Chromat polarographisch bestimmt.

REFERENCES

[1] C. E. MILLS AND S. E. HERMON, *Metallurgia*, 44 (1951) 327.
[2] F. FEIGL, *Spot Tests*, Elsevier Publishing Co., Amsterdam 1954, p. 68.
[3] J. J. LINGANE AND I. M. KOLTHOFF, *J. Am. Chem. Soc.*, 62 (1940) 852.
[4] J. J. LINGANE, *Electroanalytical Chemistry*, Interscience, New York 1953, p. 261.
[5] F. FEIGL, K. KLANFER AND L. WEIDENFELD, *Z. anal. Chem.*, 80 (1930) 5.
[6] K. K. JÄRVINEN, *Z. anal. Chem.*, 75 (1928) 1.
[7] E. SCHULEK AND A. DOSZA, *Z. anal. Chem.*, 86 (1931) 81.
[8] J. J. LINGANE AND D. G. DAVIS, *Anal. Chim. Acta*, 15 (1956) 201.
[9] E. FORNASARI AND E. GAGLIARDO, *Atti. ist. veneto sci. lettere ed arti*, 115 (1957) 217.

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STUDIES IN THE SPECTROPHOTOMETRIC DETERMINATION OF SILICON IN MATERIALS DECOMPOSED BY HYDROFLUORIC ACID

II. SPECTROPHOTOMETRIC DETERMINATION OF FLUOSILICIC ACID IN HYDROFLUORIC ACID

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INTRODUCTION

Commercially hydrofluoric acid always contains small amounts of fluosilicic acid.

Earlier procedures for the determination of fluosilicic acid in the presence of hydrofluoric acid are based on unsatisfactory volumetric methods. KOLTHOFF[1] surveys the literature on this subject. He improves the volumetric method for the determination of both acids in mixture by evaporating the hydrofluoric acid in the presence of sodium chloride and hydrochloric acid. The remaining fluosilicate is titrated with standard alkali. The end-point is, however, not sharp, and the method requires large samples for the determination of low fluosilicic acid contents.

For the determination of small amounts of silicon photometric methods are more suitable. On the basis of investigations by CASE[2], CADE[3] describes a procedure for the photometric determination of fluosilicic acid in commercial hydrofluoric acid. Most of the latter acid is separated by evaporation as recommended by KOLTHOFF. The

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small amount of hydrofluoric acid remaining is converted to fluoboric acid, and the fluosilicic acid is determined photometrically as the yellow silicomolybdic acid.

In the present paper an improved method for the spectrophotometric determination of fluosilicic acid in hydrofluoric acid is described. The silicon is determined directly as α-silicomolybdic acid without preceding evaporation of hydrofluoric acid.

Instruments, reagents and apparatus

Instruments, reagents and apparatus were the same as described in Part I of this series[4], the only exception being the use of 2.000-cm glas cells.

Experimental

For the determination of the relatively small amounts of fluosilicic acid present in commercial hydrofluoric acid (normally below 0.25%), a special calibration curve was used in which the extinction of the α-silicomolybdic acid was measured at a lower wavelength than usual. A wavelength of 370 mμ was suitable for amounts less than 1 mg SiO_2 per 100 ml.

A standard solution of silicic acid was prepared by decomposing 50.0 mg of silicon dioxide with 1.0 g of sodium carbonate, dissolving the melt in dilute hydrochloric acid and diluting to 500 ml; this solution contained 0.1 mg SiO_2 per ml.

Varying amounts of this standard solution were pipetted into plastic beakers containing about 50 ml of water. Ammonium molybdate (5 ml of 2% solution) was added and the pH adjusted to 1.0 ± 0.5. After 3 h on the boiling water bath the solutions were cooled to room temperature, transferred to 100-ml volumetric flasks and diluted to the mark. The extinction was measured at 370 mμ against a blank solution containing ammonium molybdate, adjusted to pH 1.0 ± 0.5 and heated as the sample solution.

In Table I the extinction data and the extinction indexes (E/C) are given for the series of solutions.

TABLE I

CALIBRATION CURVE FOR THE DETERMINATION OF FLUOSILICIC ACID IN HYDROFLUORIC ACID. WAVELENGTH 370 mμ. 2.000-cm CELLS

Mg SiO_2 per 100 ml	*Extinction*	*Extinction index (E/C)*
0.1	0.096	0.96
0.2	0.194	0.97
0.3	0.300	1.00
0.4	0.392	0.98
0.5	0.486	0.97
0.6	0.588	0.98
0.7	0.690	0.99
0.8	0.780	0.98

It is seen that Beer-Lambert's law is followed up to at least 0.8 mg SiO_2 per 100 ml.

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Procedure

From the hydrofluoric acid to be analyzed about 1 ml is transferred (with the teflon tube pipette or with a plastic measuring cylinder) to a weighed plastic beaker. The beaker is stoppered with a tightly fitting plastic stopper and reweighed. Then 50 ml of 25% aluminium chloride solution and 5 ml of 2% ammonium molybdate solution are added. The solution is diluted to about 90 ml with distilled water, the pH is adjusted to 1.0 ± 0.5, and the solution is heated, cooled and diluted as in the preparation of the calibration curve.

Finally the extinction is measured at 370 mμ and the content of fluosilicic acid calculated. A blank solution is prepared from the reagents and treated in the same way as the sample solution.

Analysis of commercial reagent grade hydrofluoric acid (35–40%) used in this investigation showed a content of 0.01% fluosilicic acid, which is well below the permitted maximum content of 0.25%.

Complexing agents for hydrofluoric acid

Boric acid is frequently recommended to make hydrofluoric acid harmless by the formation of slightly dissociated fluoboric acid. At the start of the present investigations a saturated solution of boric acid in water was used to complex excess of hydrofluoric acid. It was, however, observed that the extinction of solutions of α-silicomolybdic acid in volumetric flasks increased on standing, and it was concluded that this was due to attack on the glass.

The same phenomenon was not observed when aluminium chloride was used as complexing agent, and consequently this reagent was preferred.

SUMMARY

A procedure is reported for the spectrophotometric determination of fluosilicic acid in commercial hydrofluoric acid. The determination of silicon as α-silicomolybdic acid is carried out directly without previous separation of hydrofluoric acid.

RÉSUMÉ

Une méthode est proposée pour le dosage spectrophotométrique de l'acide fluosilicique dans l'acide fluorhydrique commercial.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode beschrieben zur Bestimmung von Kieselfluorwasserstoffsäure in Fluorwasserstoffsäure handelsüblicher Qualität.

REFERENCES

[1] I. M. KOLTHOFF AND V. A. STENGER, *Volumetric Analysis*, Vol. II, Second revised Ed., Interscience Publishers, Inc., New York 1947.
[2] O. P. CASE, *Anal. Chem.*, 16 (1944) 309.
[3] G. N. CADE, *Anal. Chem.*, 17 (1945) 372.
[4] F. J. LANGMYHR AND P. R. GRAFF, *Anal. Chim. Acta*, 21 (1959) 334.

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ÉTUDE DU COMPORTEMENT POLAROGRAPHIQUE DU ZIRCONIUM EN MILIEU ACIDE ET EN PRÉSENCE D'IONS NITRATE

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INTRODUCTION

En étudiant le comportement polarographique des sels de zirconium en milieu chlorhydrique, LAUBENGAYER ET EATON[1] observent une onde de réduction ayant un potentiel de demi-onde voisin de —1,65 V/E.C.S. et dépendant fortement de la concentration en ions hydrogène. Selon ces auteurs, cette onde serait la composante des ondes de réduction des ions hydrogène et zirconium. A pH 3, ils observent deux ondes distinctes; à des valeurs de pH supérieures à 4, l'une des ondes disparaît totalement.

Plus récemment, COZZI[2], parvient à séparer les deux ondes aux pH inférieurs à 3, par addition de bleu de méthylène aux solutions.

Le but du présent travail consiste à étudier le comportement polarographique du zirconium en milieu acide et en présence d'ions nitrate. En effet, les ondes observées dans ce milieu présentent des caractéristiques susceptibles d'interprétation théorique et certaines applications analytiques.

PARTIE EXPÉRIMENTALE

La liste des solutions étudiées figure au Tableau I. Le pH des solutions, contrôlé en cours de dilution à l'aide d'un pH mètre Radiometer 22, a été ajusté à l'aide de solutions d'hydroxyde de sodium ou d'acide chlorhydrique calculées de manière à atteindre un volume final de 25 ml. Des quantités différentes de nitrate de sodium ont ensuite été ajoutées au moyen de micropipettes contrôlées.

TABLEAU I

[*NaCl*]	*pH*	[ZrO^{+2}]
10^{-1} *M*	2	10^{-3} *M*
10^{-1} *M*	2	10^{-5} *M*
10^{-1} *M*	3	10^{-3} *M*
10^{-1} *M*	3	10^{-5} *M*
10^{-1} *M*	4	10^{-3} *M*
10^{-1} *M*	4	10^{-4} *M*
10^{-1} *M*	4	10^{-5} *M*

TABLEAU II

[H^+] *en M/l*	[ZrO^{+2}]	I_d *en* μA
10^{-2}	10^{-3}	150
10^{-3}	10^{-3}	15
10^{-4}	10^{-3}	3
10^{-4}	10^{-4}	0,35
10^{-2}	10^{-5}	125
10^{-3}	10^{-5}	10
10^{-4}	10^{-5}	pas d'onde
10^{-2}	10^{-7}	120

Les concentrations sont exprimées en moles/l;
les courants de diffusion sont exprimés en μA.

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Les polarogrammes ont été tracés à l'aide d'un polarographe Radiometer PO_4, à la température de 25.0° et avec un amortissement égal à 4. La constante capillaire n'a pas été déterminée, tous les polarogrammes ayant été pris dans les mêmes conditions avec le même capillaire.

RÉSULTATS EXPÉRIMENTAUX

Effet de la concentration en ions hydrogène et zirconium

Les solutions ne contenant pas de nitrates ont d'abord été polarographiées. Le Tableau II indique les valeurs du courant de diffusion de l'onde obtenue à différentes concentrations en ions hydrogène et zirconium. Aucune onde n'a été observée aux pH 5 et 6, quelle que soit la concentration en ions zirconium, de même qu'à pH 4 pour des concentrations en ions zirconium égales à 10^{-5} *M*. Des essais ont été effectués à pH 4 avec des solutions 10^{-2} *M* en ions zirconium et 1 *M* en chlorure de sodium. A ce pH et cette force ionique, on obtient un précipité d'hydroxyde de zirconium.

Dans 3 milieux: pH 4 $[ZrO^{+2}] = 10^{-3}$ *M*, pH 2 $[ZrO^{+2}] = 10^{-5}$ *M* et pH 2 $[ZrO^{+2}] = 10^{-7}$ *M*, l'onde semble se diviser en deux ondes très voisines.

Effet de la concentration en ions nitrate

Une étude générale de l'effet de la teneur en ions nitrate a ensuite été réalisée en ajoutant respectivement aux 25 ml des solutions acides de zirconium préparées, 0.1 ml de diverses solutions de nitrate de sodium. Les conditions opératoires et les résultats obtenus sont groupés dans le Tableau III. Dans certaines conditions, on observe l'apparition d'une onde supplémentaire. La Fig. 1 montre 6 courbes polarographiques obtenues dans les conditions suivantes:

TABLEAU III

	$[NO_3^-]$							
	0	$1 \cdot 10^{-7}$	$1 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	$2 \cdot 10^{-3}$
I_d pH = 2	150	—	150	150	3*	—	30*	—
$E_{\frac{1}{2}}$ $[ZrO^{+2}] = 10^{-3}$ *M*	1.58		1.60	1.63	1.14		1.14	
I_d pH = 2	125	—	125	125	125	—	125	—
$E_{\frac{1}{2}}$ $[ZrO^{+2}] = 10^{-5}$ *M*	1.57	—	1.57	1.57	1.57	—	1.57	—
I_d pH = 2	120	120	—	120	120	—	120	—
$E_{\frac{1}{2}}$ $[ZrO^{+2}] = 10^{-7}$ *M*	1.58	1.58	—	1.58	1.57	—	1.50	—
I_d pH = 3	15	15	—	0.4*	3*	6*	13*	—
$E_{\frac{1}{2}}$ $[ZrO^{+2}] = 10^{-3}$ *M*	1.53	1.53	—	1.1	1.1	1.1	1.1	
I_d pH = 3	10	10	—	10	10	—	10	—
$E_{\frac{1}{2}}$ $[ZrO^{+2}] = 10^{-5}$ *M*	1.54	1.54	—	1.54	1.54	—	1.54	—
I_d pH = 4	3	—	3	3	—	—	2*	—
$E_{\frac{1}{2}}$ $[ZrO^{+2}] = 10^{-3}$ *M*	1.52		1.52	1.48	—	—	1.0	—
I_d pH = 4	0.35	0.35	—	0.35	—	—	0.35	0.35
$E_{\frac{1}{2}}$ $[ZrO^{+2}] = 10^{-4}$ *M*	1.53	1.50		1.48	—	—	1.34	1.32

$[ZrO^{+2}] = 10^{-3}\,M$; pH $= 2$; $[NaCl] = 10^{-1}\,M$; $[NO_3^-] = 1:0$; $2:10^{-3}\,M$; $3:2\cdot10^{-3}\,M$; $4:3\cdot10^{-3}\,M$; $5:4\cdot10^{-3}\,M$; $6:6\cdot10^{-3}\,M$.

Les courants de diffusion correspondant à l'apparition d'une onde de réduction due à la présence d'ions nitrate sont marqués d'une astérisque dans le Tableau III. On constate que la hauteur totale des deux ondes est dans tous les cas approximativement constante. L'ensemble des résultats obtenus montre l'existence aux pH 2,3 et 4 d'une seconde onde de potentiel de demi-onde voisin de —1.00 V/E.C.S. Sa hauteur dépend de la concentration en ions nitrate, mais n'est jamais supérieure à celle de l'onde due aux seuls ions hydrogène et zirconium.

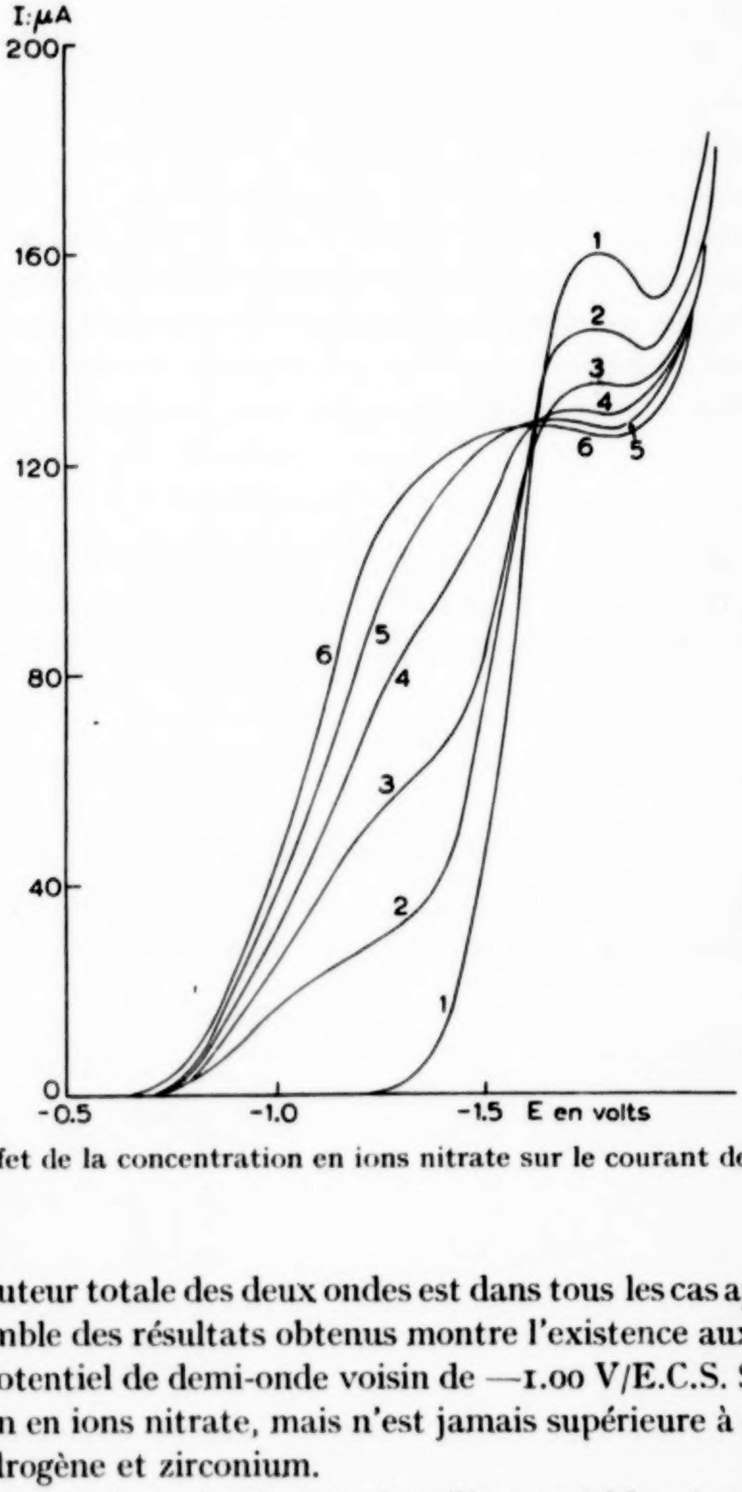

Fig. 1. Effet de la concentration en ions nitrate sur le courant de diffusion.

L'effet de la teneur en ions nitrate pour le milieu $10^{-3}\,M$ en ions zirconium à pH 2 (Tableau IV) a ensuite été étudié de manière plus précise.

L'onde de potentiel de demi-onde voisin de —1.00 V/E.C.S. est proportionnelle à la concentration en ions nitrate pour autant que la valeur du courant de diffusion soit inférieure à celle dûe aux ions hydrogène et zirconium.

Elle n'apparaît plus pour des concentrations en ions zirconium inférieures à $10^{-5}\,M$.

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Nous avons d'autre part, étudié l'effet de la teneur en ions zirconium à concentration constante en ions nitrate et hydrogène. Le Tableau V montre, à pH 2 et pour une concentration en ions nitrate égale à $1 \cdot 10^{-3}$ M, la valeur du courant limite pour des concentrations en ions zirconium $0.5 \cdot 10^{-3}$; $1 \cdot 10^{-3}$; $1.5 \cdot 10^{-3}$ et $2 \cdot 10^{-3}$ M. Le courant limite de la première onde est indépendant de la teneur en ions zirconium.

TABLEAU IV

$[NO_3^-]$ *en* $M/1$	I_{d_1}	$E^1_{\frac{1}{2}}$	I_d *total*	$E^2_{\frac{1}{2}}$
0	—	*	150	—1 62 V/E.C.S.
$1 \cdot 10^{-5}$	(0.5)	*	150	—1 62
$0.6 \cdot 10^{-4}$	1.7	*	150	—1.62
$1.1 \cdot 10^{-4}$	3.3	*	150	—1.62
$6.1 \cdot 10^{-4}$	18	*	140	—1.62
$1.11 \cdot 10^{-3}$	33	*	140	—1.60 V/E.C.S.
$1.0 \cdot 10^{-3}$	30	*	140	*
$2 \cdot 10^{-3}$	54	—1.20 V/E.C.S.	135	*
$4.5 \cdot 10^{-3}$	120	—1.30 V/E.C.S.	—	*
$7 \cdot 10^{-3}$	120	—1.20 V/E.C.S.	—	*
$1.7 \cdot 10^{-2}$	120	—1.12 V/E.C.S.	—	*
$3.7 \cdot 10^{-2}$	120	—1.05 V/E.C.S.	—	*
$7.7 \cdot 10^{-2}$	120	—1.02 V/E.C.S.	—	*

* indique une onde trop irréversible pour pouvoir déterminer $E_{\frac{1}{2}}$ avec précision.

TABLEAU V

pH = 2	$[NO_3^-] = 1 \cdot 10^{-3}$ M	
$[ZrO^{+2}]$	I_{d_1}	I_d *total*
$0.5 \cdot 10^{-3}$	30	150
$1 \cdot 10^{-3}$	30	150
$1.5 \cdot 10^{-3}$	30	150
$2 \cdot 10^{-3}$	30	150

TABLEAU VI

$[ZrO^{+2}] = 10^{-3}$ M.		$[NO_3^-] = 1 \cdot 10^{-4}$ M.	
pH	$[H^+]$	I_{d_1}	I_{d_2}
2.77	$1.70 \cdot 10^{-3}$	3	22
2.52	$3 \cdot 10^{-3}$	3	36
2.17	$6.7 \cdot 10^{-3}$	3	74
1.86	$1.4 \cdot 10^{-2}$	3	144

Enfin, les résultats groupés dans le Tableau VI montrent que si la concentration en ions nitrate vaut 10^{-4} M et la concentration en ions zirconium 10^{-3} M, le courant limite de diffusion est indépendant du pH, aux pH 2.77; 2.52; 2.17 et 1.86.

EFFET DE LA TEMPÉRATURE ET DE LA PRESSION DE LA COLONNE DE MERCURE

L'effet de la température et de la hauteur de la colonne de mercure sur le courant de diffusion est résumé dans les Tableaux VII et VIII.

DISCUSSION

L'ensemble de nos résultats expérimentaux montre qu'en milieu acide et en présence d'ions zirconium, les ions nitrate se réduisent à l'électrode à goutte de mercure. Le potentiel de demi-onde correspondant à cette réduction catalysée est voisin de —1.00

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V/E.C.S.; la hauteur de l'onde polarographique n'est pas proportionnelle à la racine carrée de la hauteur du réservoir de mercure (Tableau VII) mais le courant de diffusion dépend de la température de la même manière qu'une onde de diffusion normale (Tableau VIII), soit environ 2.5% par degré centigrade.

TABLEAU VII

Solution	*$h_1 = 70$ cm* *$\sqrt{h} = 8.37$*		*$h_2 = 55$ cm* *$\sqrt{h} = 7.42$*		*$h_3 = 40$ cm* *$\sqrt{h} = 6.33$*	
	I_{a_1}	I_{a_2}	I_{a_1}	I_{a_2}	I_{a_1}	I_{a_2}
pH = 2 $[ZrO^{+2}] = 10^{-3}\ M$	33	150	31	140	30	120
pH = 3 $[ZrO^{+2}] = 10^{-3}\ M$	—	17	—	16	—	14
pH = 2 $[ZrO^{+2}] = 10^{-5}\ M$	—	150	—	140	—	130

TABLEAU VIII

Solution	*$T = 25°$*		*$T = 35°$*	
	I_{a_1}	I_{a_2}	I_{a_1}	I_{a_2}
pH = 2 $[ZrO^{+2}] = 10^{-3}\ M$ $[NO_3^-] = 1.11 \cdot 10^{-3}\ M$	31	110	42	120

On peut rapprocher le comportement polarographique des ions nitrate en présence d'ions zirconium à celui observé pour les ions nitrate dans une solution d'ions polyvalents[3-5] tels que les ions uranium. Le schéma proposé pour cette réduction est généralement le suivant:

$$NO_3^- + 8e + 6H_2O = NH_3 + 9\ OH^-$$

ou

$$NO_3^- + 8e + 9H^+ = NH_3 + 3\ H_2O$$

La réduction des nitrates à l'électrode consommant des ions H^+, la hauteur de l'onde des nitrates ne peut dépasser une certaine valeur, fonction de la concentration en ions H^+ et UO_2^+ ou ZrO^{+2}. En effet, la quantité d'ions H^+ diminuant le pH s'élève et les ions UO_2^+ ou ZrO^{+2} précipitent.

Dans le cas de l'uranium on observe une onde de réduction des ions nitrate à —1.00 V/E.C.S., située exactement au même potentiel que la seconde onde de réduction du cation uranyle.

On a en effet:

(1) $UO_2^{+2} + e = UO_2^+$ $E_{\frac{1}{2}} = -0.20$ V/E.C.S.

(2) $UO_2^+ + 2e = U^{+3} + 2O^{-2}$ $E_{\frac{1}{2}} = -1.00$ V/E.C.S.

La réduction des nitrates serait donc catalysée par le cation UO_2^+ ou U^{+5}.

Pour le zirconium, ce serait le cation ZrO^{+2} ou Zr^{+4} qui catalyserait la réaction.

La charge des cations U^{+5} et Zr^{+4} étant plus importante que celle des cations UO_2^+ et ZrO^{+2}, on peut faire l'hypothèse que ce sont effectivement eux, qui à l'électrode, jouent le rôle de catalyseur. En effet, on peut montrer que la concentration à une distance δ de la surface de l'électrode correspondant au centre de gravité des charges attirées par l'électrode (plan δ) peut être beaucoup plus grande en cations fortement chargé, qu'au sein de la solution. Dans le cas du zirconium, si la distribution du dépolarisant reste boltzmannienne jusqu'au plan δ, ce rapport serait donné par:

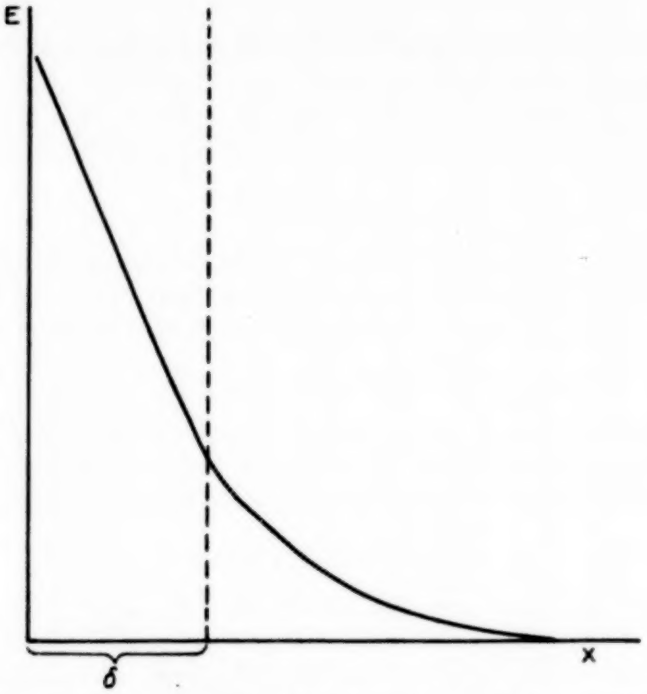

Fig. 2. Distribution du potentiel dans la double couche ionique.

$$\log \frac{(Zr^{+4})\delta}{(Zr^{+4})\ \text{sol}} = \frac{-1}{2.31}\ \frac{ZF}{RT}\ \psi = \frac{-4}{0.059}\ \psi = \frac{-4}{0.059}\ (-10^{-1}) \approx 8$$

D'où:

$$\frac{(Zr^{+4})\delta}{(Zr^{+4})\ \text{sol}} \approx 10^8$$

où ψ, de l'ordre de -10^{-1}, est le potentiel relatif a une distance δ de l'électrode. Le potentiel ψ peut être calculé en fonction de la charge de l'électrode. Les détails de ces calculs sont décrits par L. GIERST[6].

Si la réaction $ZrO^{+2} + 2\ H^+ = Zr^{+4} + H_2O$ peut se produire, il peut y avoir accumulations d'ions Zr^{+4} à l'électrode. Le cation Zr^{+4} formé pourrait alors, à l'électrode, catalyser la réduction des nitrates. Nous avons vérifié expérimentalement cette hypothèse à l'aide des solutions suivantes (Fig. 3):

1) Sol. $2 \cdot 10^{-3}\ M$ en ZrO^{+2}, $2 \cdot 10^{-2}\ M$ en H^+, $2 \cdot 10^{-3}\ M$ en NO_3^-, $(H^+) + (Na^+) = C^{te} = 1.1 \cdot 10^{-1}\ M$.

2) Sol. $2 \cdot 10^{-3}\ M$ en ZrO^{+2}, $10^{-2}\ M$ en H^+, $2 \cdot 10^{-3}\ M$ en NO_3^-, $(H^+) + (Na^+) = C^{te} = 1.1 \cdot 10^{-1}\ M$.

3) Sol. $10^{-3}\ M$ en ZrO^{+2} et $2 \cdot 10^{-2}\ M$ en H^+, $2 \cdot 10^{-3}\ M$ en NO_3^-, $(H^+) + (Na^+) = C^{te} = 1.1 \cdot 10^{-1}\ M$.

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4) Sol. 10^{-3} *M* en ZrO^{+2} et $4 \cdot 10^{-2}$ *M* en *H*$^+$, $2 \cdot 10^{-3}$*M* en NO_3^-, $(H^+) + (Na^+) = C^{te} = 1.1 \cdot 10^{-1}$ *M*.

5) Sol. 10^{-3} *M* en ZrO^{+2} et $8 \cdot 10^{-2}$ *M* en H^+, $2 \cdot 10^{-3}$ *M* en NO_3^-, $(H^+) + (Na^+) = C^{te} = 1.1 \cdot 10^{-1}$ *M*.

On observe que la courbe correspondant à la solution 4 correspond parfaitement avec celle de la solution 2.

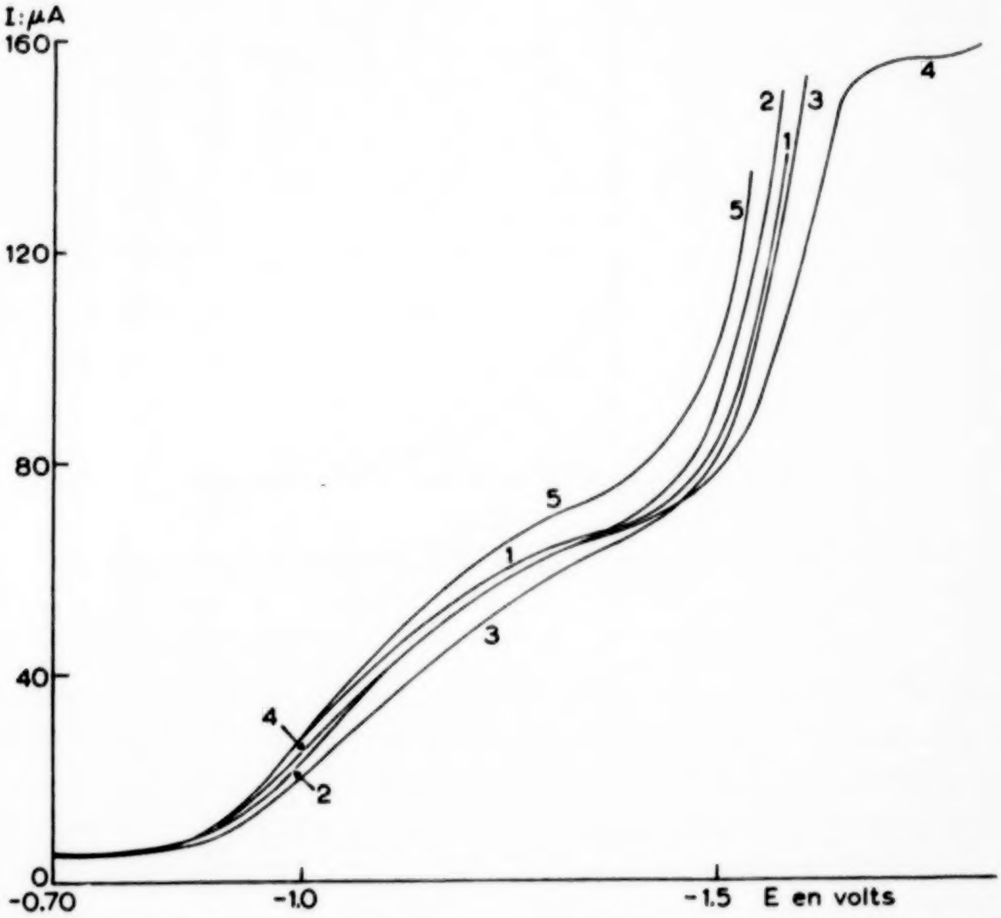

Fig. 3. Effet de la concentration en ions hydrogène sur le courant de diffusion.

Par contre, la solution 3 donne une onde située en dessous de celle de la solution 2, tandis que la solution 5 donne une onde située au-dessus.

On voit donc, en examinant les ondes polarographiques obtenues, que la réduction des nitrates s'opère à l'aide d'un mécanisme d'ordre deux en H^+ par rapport au zirconium.

Ceci confirme donc l'hypothèse que l'accumulation des ions Zr^{+4} se produit effectivement à l'électrode et que ce sont vraisemblablement les ions Zr^{+4} et non ZrO^{+2} qui catalysent la réduction des ions nitrates.

CONCLUSION

La réduction des nitrates à l'électrode à goutte est catalysée par les ions Zr^{+4} produits en milieu acide selon la réaction $ZrO^{+2} + 2 H^+ = Zr^{+4} + H_2O$ et accumulés à l'électrode. Cette hypothèse a été vérifiée expérimentalement. L'onde de réduction obtenue peut servir au dosage quantitatif des ions nitrate lorsque leur concentration varie entre $1 \cdot 10^{-5}$ et $5 \cdot 10^{-3}$ *M* à pH 2 si la teneur en ions zirconyle est voisine de 10^{-3}*M*.

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REMERCIEMENTS

Nous tenons à remercier M. L. Gierst, chef de travaux à l'Université de Bruxelles des suggestions qu'il nous a données pour l'interprétation de nos résultats.

RÉSUMÉ

On observe, en présence de zirconium, une onde de réduction catalytique des ions nitrate, à l'électrode à goutte de mercure. Cette onde peut servir au dosage quantitatif des ions nitrate. On donne, en outre, le mécanisme du processus de réduction.

SUMMARY

In the presence of zirconium, one observes a catalytic reduction wave of nitrate ions at the mercury dropping electrode. This wave can be used for the quantitative determination of nitrate ions. The mechanism of the reduction is explained.

ZUSAMMENFASSUNG

In Gegenwart von Zirkonium geben Nitrat-Ionen an der Quecksilbertropfelektrode eine Welle, die eine katalytische Reduktion anzeigt. Diese Welle kann zur quantitativen Bestimmung von Nitrat-Ionen verwendet werden. Eine Erklärung für den Mechanismus der Reduktion ist gegeben.

BIBLIOGRAPHIE

[1] A. W. Laubengayer et R. B. Eaton, *J. Am. Chem. Soc.*, 62 (1940) 2704.

[2] D. Cozzi, *Proc. Intern. Congr. Pure and Appl. Chem.*, 11 (1947) 57.

[3] A. Rylich, *Collection Czechoslov. Chem. Communs*, 7 (1935) 288.

[4] M. Tokuoka et J. Ruzicka, *Collection Czechoslov. Chem. Communs*, 6 (1934) 339.

[5] I. M. Kolthoff, W. E. Harris et G. Matsuyana, *J. Am. Chem. Soc.*, 66 (1944) 1782.

[6] L. Gierst, *Thèse d'agrégation de l'enseignement supérieur*, U.L.B. 1958, p. 73.

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THE CHARACTERIZATION AND IDENTIFICATION OF THE RARE-EARTH CHLORIDE HYDRATES BY DIFFERENTIAL THERMAL ANALYSIS

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Although there are a number of techniques that can be used to identify the rare-earth elements, a simple and convenient method, differential thermal analysis (DTA), has long been neglected. By this method, the qualitative identification of a rare-earth compound is possible by determining the temperatures at which exothermic (exotherms) or endothermic (endotherms) reactions take place as the substance is heated[1]. Under similar conditions of sample size and packing, furnace heating rate, and type of recorder, these exotherm and endotherm temperature maximas are reproducible enough so as to be useful for the identification of a series of rare-earth compounds. This method is valuable for the identification of the individual rare-earths or, in certain cases, for mixtures of them.

For our first investigation, the thermal decomposition of all of the rare-earth chloride hydrates (except Pm) were studied by DTA. The metal chlorides were in the form of the 6- or 7-hydrates and were the same compounds that had previously been studied on the thermobalance[2,3].

EXPERIMENTAL

Reagents

The rare-earth compounds were obtained in the form of their oxides of 99.9% purity from Research Chemicals, Inc., Burbank, Calif., and the Lindsay Chemical Co., West Chicago, Ill. The purity was that listed by the supplier.

Preparation of salts

The rare-earth chloride hydrates were prepared as previously described[1].

DTA apparatus

The apparatus consisted of a stainless steel sample holder and furnace; a motor-driven variable transformer to control the furnace heating rate; and a strip-chart microvolt recorder[4]. The differential temperatures were measured with 28 gauge platinum—90% platinum—10% rhodium thermocouples. Sample sizes ranged in weight from 0.200 to 0.215 g and were mixed with ignited alumina in a 1:1 ratio; ignited alumina was also used in the reference chamber. The furnace heating rate was about 10.5° per min. Thermograms were recorded on 5 in. wide chart paper using a chart speed of 6 in. per h.

DISCUSSION

The thermograms of the rare-earth chloride hydrates are given in Figs. 1–3. The prominent endotherm maxima temperatures are given in Table I.

On the basis of the thermograms, it is convenient, for purposes of discussion, to classify the thermal decomposition patterns into 4 main groups: Group I—La, Ce, Pr, and Nd; Group II—Sm, Eu, and Gd; Group III—Tb, Dy, Y, Ho, Er, and Tm; Group IV—Yb and Lu. These groups are just arbitrary but unpublished results on the thermal decomposition of the rare-earth nitrate hydrates reveal much the same classification.

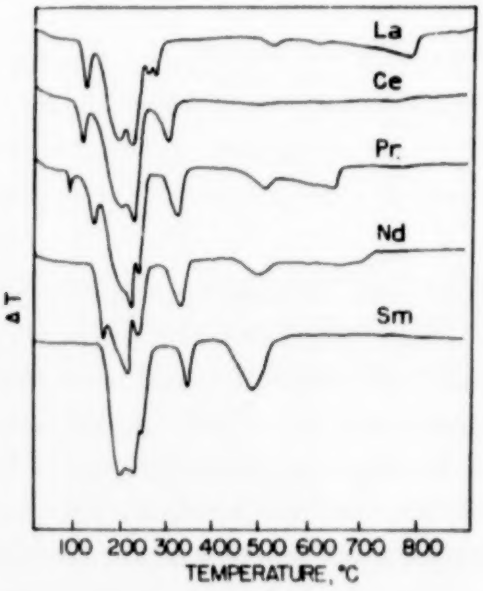

Fig. 1. Thermograms of the rare-earth chloride hydrates. Lanthanum to samarium.

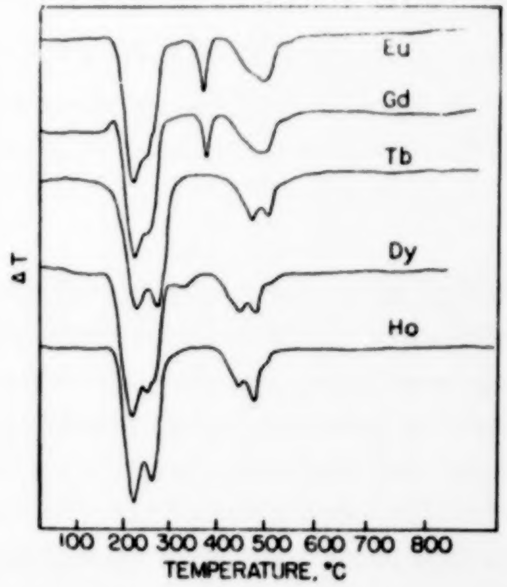

Fig. 2. Thermograms of the rare-earth chloride hydrates. Europium to holmium.

Group I

In this group, the thermograms are characterized by one or two small endotherms which preceed the large dehydration endotherms. These small endotherms are thought to arise from the heat absorbed by the partial fusion of the metal salts. Also observed in this group, with the exception of cerium, are the endotherms in the 400°–650° temperature range. It is known from thermobalance studies[1] that the terminal thermal decomposition products are the metal oxychlorides and these endotherms are presumed to be due to their formation. As the atomic weight of the rare-earth metal ion increased, the metal oxychlorides were obtained at progressively lower temperatures; this could explain the disappearance of these endotherms in the other groups studied.

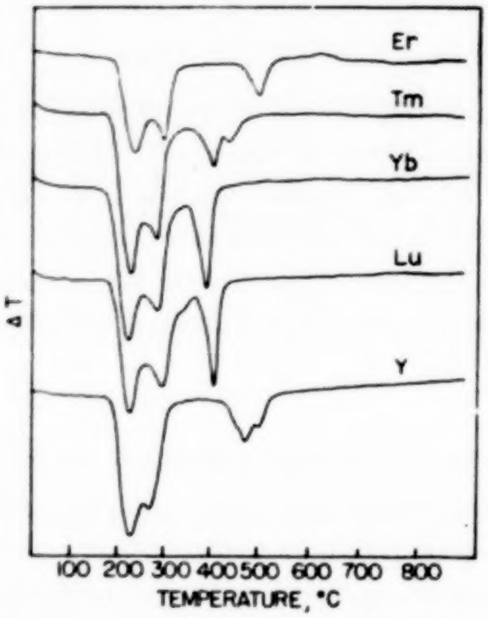

Fig. 3. Thermograms of the rare-earth chloride hydrates. Erbium to yttrium.

TABLE I

MAXIMA TEMPERATURES FOR THE ENDOTHERMS OF THE RARE-EARTH CHLORIDE HYDRATES

Rare-earth salt	*Temperature, °C*						
$LaCl_3.7H_2O$	110	163	190	215	430	650	
$CeCl_3.6H_2O$	100	170	185	250			
$PrCl_3.7H_2O$	75	120	180	190	260	410	525
$NdCl_3.6H_2O$	135	175	190	270	400		
$SmCl_3.6H_2O$	160	190	275	390			
$EuCl_3.6H_2O$	180	295	400				
$GdCl_3.6H_2O$	180	300	390				
$TbCl_3.6H_2O$	180	220	380	405			
$DyCl_3.6H_2O$	175	205	355	385			
$HoCl_3.6H_2O$	175	210	350	380			
$ErCl_3.6H_2O$	190	240	400				
$TmCl_3.6H_2O$	180	255	320	350			
$YbCl_3.6H_2O$	180	227	310				
$LuCl_3.6H_2O$	180	235	325				
$YCl_3.6H_2O$	185	220	380				

Group II

In this group, the large dehydration endotherms consisted entirely of just one maxima with several small endotherm shoulders. There were sharp endotherms in the 160°–180° temperature range and broad endotherms in the 390°–400° temperature range. The latter are presumed to be due to the formation of the metal oxychlorides; thermobalance studies appear to confirm this.

Group III

By far the largest group, this group is characterized by the splitting of the dehydration endotherms into two maximas and also the splitting of the oxychloride formation endotherms. The splitting of the former resulted in the formation of maximas in the 175°–190° and the 205°–240° temperature range. It is interesting to observe that the thermogram for yttrium appears to fit nicely between dysprosium and holmium, in agreement with results found from separation studies[5].

Group IV

In this group, the splitting of the dehydration endotherms were again observed but new endotherms appeared in the 310°–325° temperature range. These new endotherms were characterized by their rather sharp, narrow appearance; in contrast to the broad endotherms found in this region in the Group III compounds.

SUMMARY

The thermal decomposition of all of the rare-earth chloride hydrates was studied by differential thermal analysis. By use of the resulting thermograms, it is possible to apply this method as a means of identification of the individual rare-earth elements. The endotherm temperature maximas are recorded and discussed for all of the rare-earth compounds.

RÉSUMÉ

Une étude sur la décomposition thermique des chlorures de terres rares hydratés a été effectuée par l'analyse thermique différentielle. Les thermogrammes obtenus peuvent être utilisés pour l'identification de ces éléments.

ZUSAMMENFASSUNG

Die thermische Zersetzung der Chlorid-Hydrate aller seltenen Erden wurden mit Hilfe differential-thermoanalytischer Methoden untersucht. Die erhaltenen Thermogramme ermöglichen die Identifizierung der einzelnen seltenen Erden.

REFERENCES

[1] W. J. Smothers and Y. Chiang, *Differential Thermal Analysis: Theory and Practice*, Chemical Publishing Co., New York 1958.
[2] W. W. Wendlandt, *J. Inorg. & Nuclear Chem.*, 5 (1957) 118.
[3] W. W. Wendlandt, *J. Inorg. & Nuclear. Chem.*, 9 (1959) 136.
[4] W. W. Wendlandt, to be published.
[5] D. M. Yost, H. Russell and C. S. Garner, *The Rare-Earth Elements and Their Compounds*, John Wiley and Sons, Inc., New York 1947, p. 41.

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THE CONDUCTOMETRIC TITRATION OF CARBOXYLIC AND PHENOLIC ACIDS IN NON-AQUEOUS SOLUTIONS

III. THE RESOLUTION OF ACID MIXTURES AND SOME PRACTICAL APPLICATIONS

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INTRODUCTION

During preliminary investigations on the conductometric determination of acids[1] it was observed that when certain dibasic compounds were titrated in pyridine or dimethylformamide (DMF) with a quaternary ammonium base, an N-shaped titration curve with two distinct equivalence points was obtained. Other dibasic acids gave, under the same conditions, a chair-shaped curve with less distinct end-points. The titration of monobasic acids was the least satisfactory; in general only slight breaks were observed in the conductance curves.

From the results described previously[1] and also from the high-frequency titrations under similar conditions described by ISHIDATE AND MASUI[2], it was expected that suitable mixtures of acids could be resolved by conductometric titration, especially those consisting of a monobasic acid and a dibasic acid giving an N-shaped curve. In addition it should be possible to resolve some binary mixtures of dibasic acids.

From the foregoing it is clear that the results are primarily determined by the accuracy with which the dibasic acids can be titrated. The optimum conditions for these acids were studied in the second paper of this series[3], the strong influence of solvent and base being discussed. The best results were obtained in media of low solvating power, *e.g.* pyridine, DMF and, to a less extent, propanol-2 and methanol–benzene mixtures. A low dielectric constant, *i.e.* below 20, also improved the results, although under these circumstances complications arose owing to the strongly decreasing conductance of the solutions[3]. As to the bases used, it was found that titration of dibasic acids could be carried out with titrants derived from small cations (K^+, $(CH_3)_4N^+$) and with amines in solvents containing alcohol, or better, with tetrabutylammonium hydroxide in DMF or pyridine.

The titrations described in the present paper were mainly done under the optimum conditions found in the preceding investigations and the present results pertain only to these conditions. In the same way we have restricted ourselves to titrations at room temperature, although higher temperatures might be favourable[3]. In spite of these limitations, the investigation gives an idea of the possibilities of conductometric titration of acid mixtures in non-aqueous media.

EXPERIMENTAL

Titrants and solvents

The bases used were potassium methoxide in pyridine–benzene, and tetramethyl- and tetrabutylammonium hydroxide in methanol–benzene. For the preparation of these titrants, see the first paper of this series[1]. The strength of the bases varied between 0.1 and 0.3 *N*.

The solvents used were methanol, pyridine and dimethylformamide. In addition, mixtures of one or two of these solvents with benzene or xylene were sometimes applied. All the solvents were of reagent grade and contained only minor quantities of water (0.1–0.5%).

Electrical equipment

The resistance measurements were carried out with the same instruments as previously described[1,3]. A relative accuracy of ± 0.5% proved to be sufficient for our purpose.

Titration procedure

The acid mixtures were weighed accurately in 5-ml beakers (tall form) in such quantities that 1–2 ml of base was required per acid group to be determined. Then the volume was made up to 25–50 ml, the electrode assembly inserted and the magnetic stirrer started. The titrant was added by means of a 10-ml burette in 0.1-ml portions, the equilibrium reading of the bridge being taken after each addition.

DISCUSSION OF RESULTS

1. Binary mixtures of carboxylic acids

The following binary mixtures of carboxylic acids were titrated:

a. a mono- and a dibasic acid in methanol (Table I), b. a mono- and a dibasic acid in dimethylformamide (Table II), c. a mono- and a dibasic acid in pyridine or DMF–benzene (1:3 v/v) (Table III), d. two dibasic acids in non-solvating media (Table IV).

a. A mono- and a dibasic acid in methanol

From the results given in Table I it can be seen that in principle resolution is possible for those mixtures in which the dibasic acid has a high K_1/K_2 ratio[3] in water.

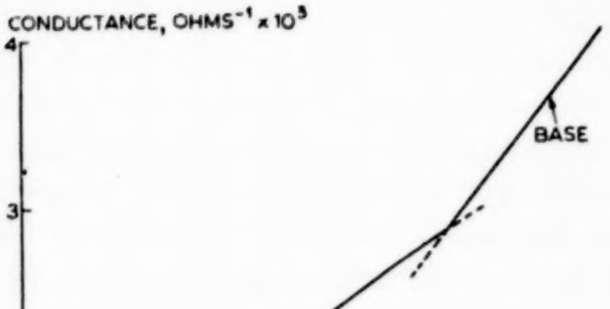

Fig. 1. Titration of a mixture of acetic acid and oxalic acid in methanol with tetramethylammonium hydroxide.

Hence, only oxalic, malonic, maleic and phthalic acid can be determined in methanol in the presence of a monobasic acid. However, the accuracy with which the end-points can be estimated in this solvent is not high (dibasic acids give only chair-shaped curves in methanol), as shown in Fig. 1. In this example the first equivalence point corresponds to the neutralization of one carboxyl group of the oxalic acid and the second to that of the other carboxyl group of the dibasic acid plus the monobasic acid. In general, the sequence of the titration is first the monobasic acid plus one function of the dibasic acid, followed by the second function of the dibasic compound.

TABLE I

TITRATION OF A MONO- AND A DIBASIC ACID IN METHANOL

Monobasic compound	*Dibasic compound*	*Base*	*Number of equivalence points*	*Resolution possible (+) or impossible (−)*
acetic acid	oxalic acid	Me_4NOH[a]	2	+
acetic acid	malonic acid	Me_4NOH	2	+
acetic acid	fumaric acid	Me_4NOH	1	—
acetic acid	maleic acid	Me_4NOH	3	+
acetic acid	tartaric acid	Me_4NOH	1	—
benzoic acid	oxalic acid	Me_4NOH	2	+
benzoic acid	malonic acid	Me_4NOH	2	+
benzoic acid	succinic acid	Me_4NOH	1	—
benzoic acid	tartaric acid	Me_4NOH	1	—
benzoic acid	phthalic acid	Me_4NOH	2	+
benzoic acid	isophthalic acid	Me_4NOH	1	—
salicylic acid	oxalic acid	Me_4NOH	2	+
salicylic acid	tartaric acid	Ne_4NOH	1	—
salicylic acid	phthalic acid	Me_4NOH	2	+
salicylic acid	isophthalic acid	Me_4NOH	1	—

[a] Me_4NOH = tetramethylammonium hydroxide

b. A mono- and a dibasic acid in DMF

In DMF the titration curve of dibasic acids has a more pronounced chair shape than in methanol and in some cases even N-shapes may be obtained (maleic and phthalic acid). Thus the accuracy of the titrations is better in DMF than in methanol, and the possibilities of resolving a binary mixture are greater. This follows from a comparison of the results given in Tables I and II. For instance, a mixture of salicylic and isophthalic acids can be resolved in DMF, but not in methanol.

As a consequence of the low solvating power of DMF, precipitate formation may be expected in some cases (*e.g.* with oxalic and fumaric acid) when bases with small cations are used. In general, precipitate formation does not affect the accuracy of the end-point, but the time required for a titration usually increases because of the rather slow precipitation in non-aqueous media.

Fig. 2 shows the titration curve of an acid mixture in DMF. It is clear that the end-points can be determined with greater accuracy than in Fig. 1. The first equivalence point corresponds to the neutralization of the caproic acid plus one function of the succinic acid and the second function of the dibasic acid is titrated between the first and the second end-points.

TABLE II

TITRATION OF A MONO- AND A DIBASIC ACID IN DIMETHYLFORMAMIDE

Monobasic compound	*Dibasic compound*	*Base*	*Number of equivalence points*	*Resolution possible(+) or impossible(−)*	*Remarks*
acetic acid	oxalic acid	Me_4NOH	1	—	precipitate
acetic acid	malonic acid	Me_4NOH	2	+	
acetic acid	succinic acid	Me_4NOH	2	+	
acetic acid	fumaric acid	Me_4NOH	—	—	precipitate
acetic acid	maleic acid	Me_4NOH	2	+	
acetic acid	tartaric acid	Me_4NOH	1	—	
caproic acid	succinic acid	Me_4NOH	2	+	
benzoic acid	oxalic acid	Me_4NOH	2	+	precipitate
benzoic acid	malonic acid	Me_4NOH	3	+	
benzoic acid	succinic acid	Me_4NOH	2	+	
benzoic acid	tartaric acid	Me_4NOH	1	—	
benzoic acid	phthalic acid	Me_4NOH	3	+	
benzoic acid	isophthalic acid	Me_4NOH	1	—	
salicylic acid	oxalic acid	Me_4NOH	2	+	precipitate
salicylic acid	tartaric acid	Me_4NOH	2	+	
salicylic acid	phthalic acid	Me_4NOH	2	+	
salicylic acid	isophthalic acid	Me_4NOH	2	+	

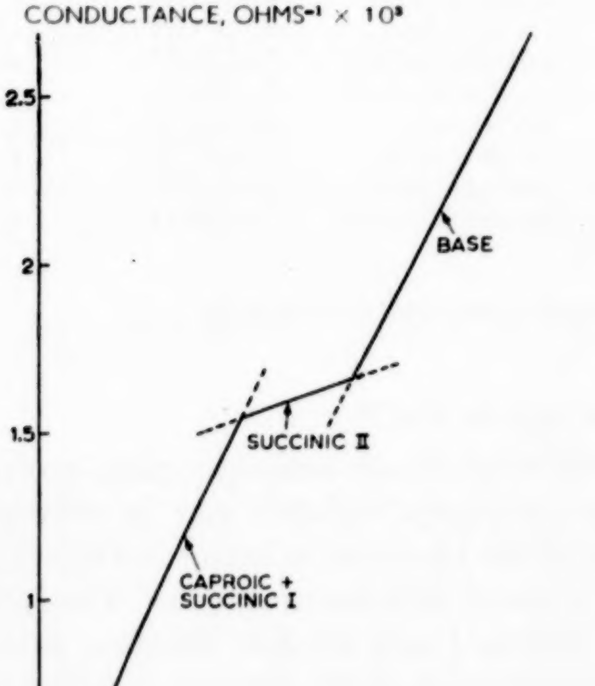

Fig. 2. Titration of a mixture of caproic acid and succinic acid in DMF with tetramethylammonium hydroxide.

c. A mono- and a dibasic acid in pyridine or DMF–benzene (1:3 v/v)

Most of the titrations were carried out in pyridine or in a DMF–benzene mixture (1:3 v/v); these have the same dielectric constant and solvating power. With a few exceptions resolution of suitable mixtures is possible by means of both tetramethylammonium hydroxide and tetrabutylammonium hydroxide. The former base generally gives insoluble neutral tetramethylammonium salts of dibasic acids, but, as in the case of pure DMF, this does not affect the analytical results.

Figures 3 and 4 give examples of resolving titrations in pyridine. In most cases the monobasic acid and the first acidic proton of the dibasic acid are titrated together (Fig. 3), but three equivalence points may also be found (Fig. 4). In this case the first and third end-point correspond to the neutralization of the dibasic compound and the second to that of the monobasic acid (see also under d). (Salicylic acid, when titrated with a quaternary ammonium base, behaves as a monobasic acid; see also under 2).

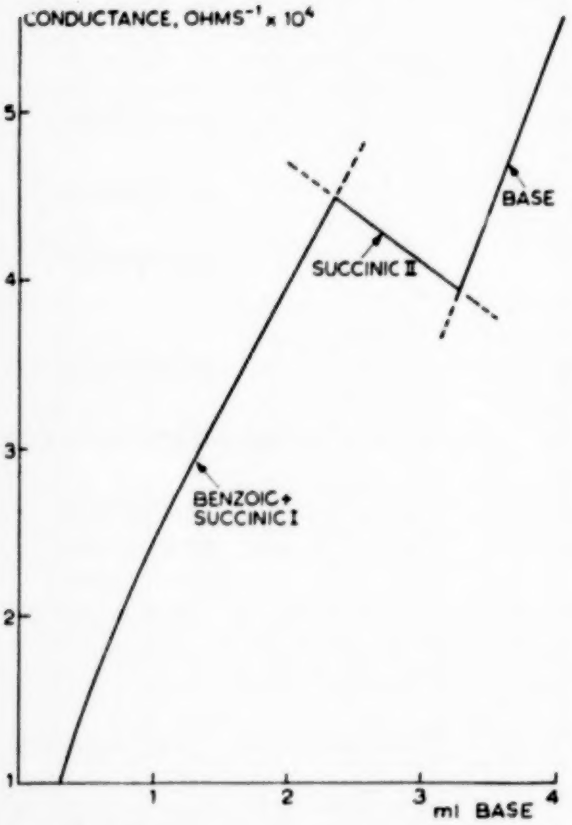

Fig. 3. Titration of a mixture of benzoic acid and succinic acid in pyridine with tetrabutylammonium hydroxide.

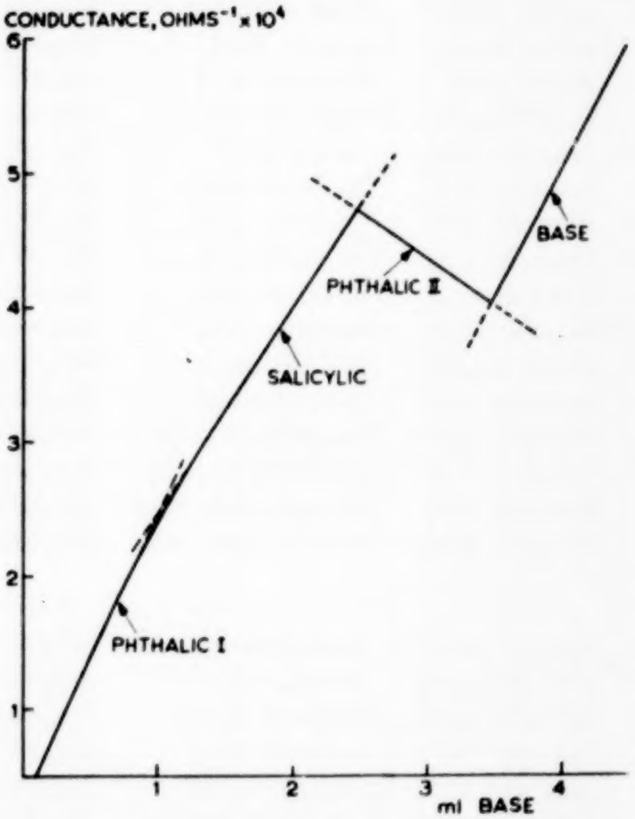

Fig. 4. Titration of a mixture of salicylic acid and phthalic acid in pyridine with tetrabutylammonium hydroxide.

When the data given in Table III are compared with those in Tables I and II, it is clear that pyridine and DMF–benzene mixtures are to be preferred for the conductometric titration of mixtures of organic acids, especially when tetrabutylammonium hydroxide is used as the base (*cf.* the results obtained by VAN DER HEIJDE[4] in potentiometric titrations of organic acids and those obtained by CUNDIFF AND MARKUNAS[5] for mixtures of strong inorganic acids).

In the resolution of acid mixtures in non-solvating media of low dielectric constant, better results can sometimes be obtained when other solvent compositions are used instead of those mentioned above. Thus, mixtures of pyridine and DMF or of pyridine and benzene are in some cases to be preferred (*cf.* resolution of benzoic–isophthalic acid and benzoic–terephthalic acid, Table III).

It should be borne in mind that the limiting ratio of the two compounds in a mixture that can be resolved conductometrically is the same as for potentiometric

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TABLE III

TITRATION OF A MONO- AND A DIBASIC ACID IN PYRIDINE OR DMF–BENZENE(XYLENE) (1:3 v/v)

Monobasic compound	*Dibasic compound*	*Base*	*Number of equivalence points*	*Resolution possible(+) or impossible(−)*	*Remarks*
acetic acid	oxalic acid	Me_4NOH	1	—	precipitate
acetic acid	oxalic acid	Bu_4NOH[a]	2	+	
acetic acid	malonic acid	Me_4NOH	3	+	precipitate
acetic acid	malonic acid	Bu_4NOH	3	+	
acetic acid	succinic acid	Me_4NOH	—	—	precipitate
acetic acid	fumaric acid	Me_4NOH	1	—	
acetic acid	maleic acid	Me_4NOH	3	+	precipitate
acetic acid	maleic acid	Bu_4NOH	2	+	
acetic acid	tartaric acid	Bu_4NOH	2	+	
caproic acid	succinic acid	Me_4NOH	—	—	precipitate
benzoic acid	oxalic acid	Bu_4NOH	3	+	
benzoic acid	malonic acid	Me_4NOH	3	+	precipitate
benzoic acid	malonic acid	Bu_4NOH	3	+	
benzoic acid	succinic and	Me_4NOH	2	+	precipitate
benzoic acid	succinic acid	Bu_4NOH	2	+	
benzoic acid	tartaric acid	Bu_4NOH	1	—	
benzoic acid	phthalic acid	Me_4NOH	3	+	precipitate
benzoic acid	phthalic acid	Bu_4NOH	3	+	
benzoic acid	isophthalic acid	Me_4NOH	2	+	pyr.–DMF (4:1 v/v)
benzoic acid	isophthalic acid	Bu_4NOH	1	—	
benzoic acid	terephthalic acid	Me_4NOH	—	—	precipitate
benzoic acid	terephthalic acid	Me_4NOH	2	+	precipitate (pyr.–benzene (4:1 v/v)
benzoic acid	terephthalic acid	Bu_4NOH	1	—	
salicylic acid	oxalic acid	Bu_4NOH	2	+	
salicylic acid	malonic acid	Bu_4NOH	2	+	
salicylic acid	succinic acid	Bu_4NOH	2	+	
salicylic acid	tartaric acid	Bu_4NOH	2	+	
salicylic acid	phthalic acid	Me_4NOH	2	+	precipitate
salicylic acid	phthalic acid	Bu_4NOH	3	+	
salicylic acid	isophthalic acid	Bu_4NOH	2	+	
salicylic acid	terephthalic acid	Bu_4NOH	2	+	
p-isopropylbenzoic acid	terephthalic acid	Me_4NOH	2	+	precipitate (pyr.–benzene (2:1 v/v)

[a] Bu_4NOH = tetrabutylammonium hydroxide

titrations, *viz.* 1:10 (equiv./equiv.). Optimum results can only be expected when both compounds are present in approximately equal amounts.

d. Two dibasic acids in non-solvating media

In general the principal condition which must be fulfilled in order to resolve a mixture of two dibasic acids is that one of the compounds should give an N-shaped titration curve and the other a chair-shaped one. It is not important whether this difference in shape is obtained with or without the aid of precipitate formation (Figs. 5 and 6), the extent of the difference determining the success of the titration.

TABLE IV

TITRATION OF TWO DIBASIC ACIDS IN NON-SOLVATING MEDIA

Compound A	*Compound B*	*Base*	*Solvent*	*Number of equivalence points*	*Resolution possible(+) or impossible(−)*	*Remarks*
oxalic acid	succinic acid	Me_4NOH	DMF	3	+	precipitate
oxalic acid	succinic acid	Bu_4NOH	pyridine	2	—	
oxalic acid	adipic acid	Me_4NOH	DMF	2	—	precipitate
oxalic acid	adipic acid	Bu_4NOH	pyridine	1	—	
oxalic acid	fumaric acid	Me_4NOH	DMF	2	—	precipitate
oxalic acid	fumaric acid	Bu_4NOH	pyridine	3	+	
oxalic acid	maleic acid	Me_4NOH	DMF	3	+	precipitate
oxalic acid	maleic acid	Bu_4NOH	pyridine	2	—	
oxalic acid	isophthalic acid	Bu_4NOH	pyridine	3	+	
succinic acid	maleic acid	Me_4NOH	DMF	3	+	
succinic acid	maleic acid	Bu_4NOH	pyridine	2	—	
adipic acid	maleic acid	Me_4NOH	DMF	2	—	
adipic acid	maleic acid	Bu_4NOH	pyridine	4	+	
adipic acid	phthalic acid	Bu_4NOH	pyridine	3	+	
fumaric acid	maleic acid	Me_4NOH	DMF	3	+	
fumaric acid	maleic acid	Me_4NOH	pyridine	3	+	precipitate
fumaric acid	maleic acid	Bu_4NOH	pyridine	3	+	
fumaric acid	isophthalic acid	Me_4NOH	DMF	1 (2)	— (+)	
fumaric acid	isophthalic acid	Bu_4NOH	pyridine	2	—	
maleic acid	isophthalic acid	Me_4NOH	DMF	3	+	
maleic acid	isophthalic acid	Me_4NOH	pyridine	3	+	precipitate
maleic acid	isophthalic acid	Bu_4NOH	pyridine	3	+	
phthalic acid	adipic acid	Bu_4NOH	pyridine	3	+	
phthalic acid	isophthalic acid	Bu_4NOH	pyridine	3	+	
phthalic acid	isophthalic acid	Bu_4NOH	pyridine–benzene	3	+	precipitate
phthalic acid	isophthalic acid	Bu_4NOH	pyridine–DMF–benzene	3	+	
phthalic acid	isophthalic acid	Me_4NOH	pyridine–benzene	3	+	
phthalic acid	isophthalic acid	Me_4NOH	pyridine–DMF–benzene	3	+	precipitate
phthalic acid	terephthalic acid	Bu_4NOH	pyridine	3	+	
phthalic acid	terephthalic acid	Bu_4NOH	pyridine–benzene	3	+	precipitate
phthalic acid	terephthalic acid	Me_4NOH	pyridine–benzene	1	—	precipitate
phthalic acid	terephthalic acid	Bu_4NOH	pyridine–DMF–benzene	3	+	
phthalic acid	terephthalic acid	Me_4NOH	pyridine–DMF–benzene	3	+	precipitate
isophthalic acid	oxalic acid	Bu_4NOH	pyridine	3	+	
isophthalic acid	maleic acid	Me_4NOH	DMF	3	+	
isophthalic acid	terephthalic acid	Bu_4NOH	pyridine–DMF–benzene	2	—	
isophthalic acid	terephthalic acid	Me_4NOH	pyridine–DMF–benzene	3	+	precipitate

Resolution requires that at least 3 equivalence points can be determined (Table IV), of which the first corresponds to the half-neutralization of both compounds and the second and third to the titration of the second functions of the respective acids. Fig. 5 gives an example of such a titration curve. At the first equivalence point the first acid groups of both oxalic and succinic acid are neutralized. Then the second acid group of oxalic acid is titrated with the formation of a sparingly soluble neutral salt. Finally, the third end-point corresponds to the neutralization of the remaining acid group of the succinic acid.

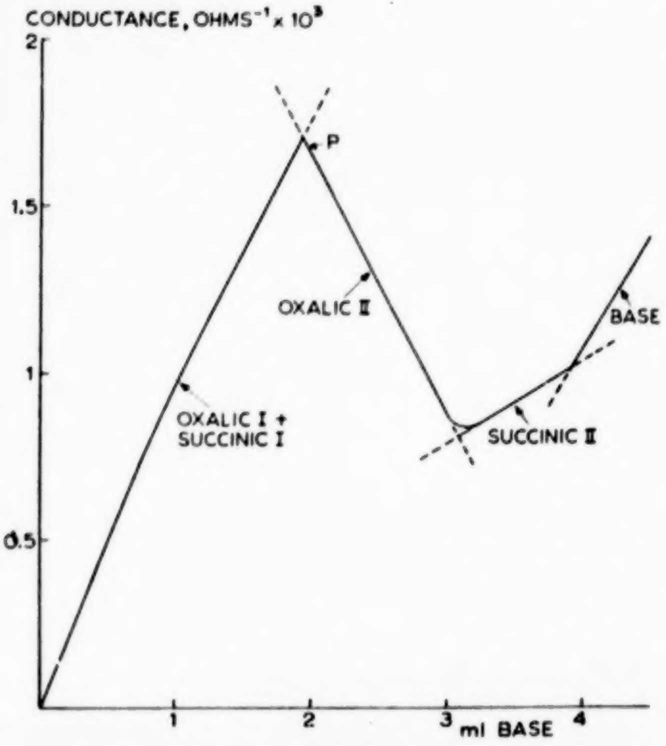


Fig. 5. Titration of a mixture of oxalic acid and succinic acid in DMF with tetramethylammonium hydroxide. (p = precipitate formation)

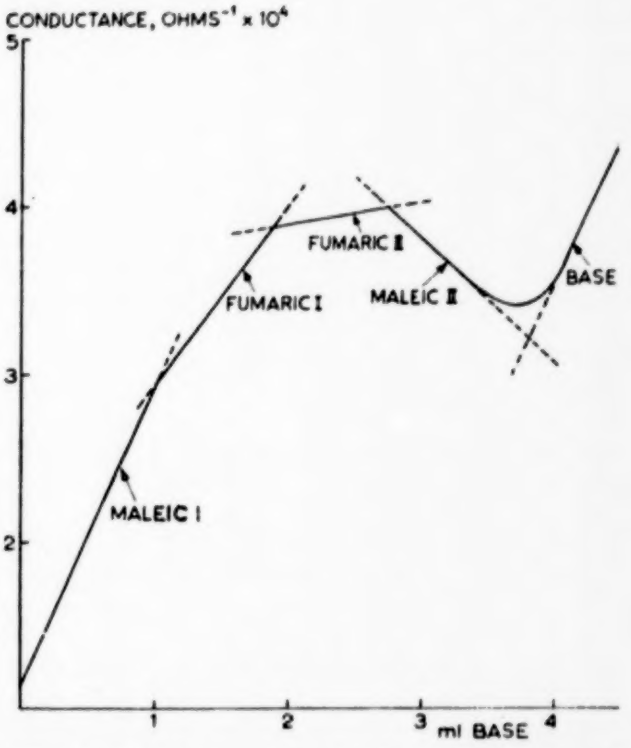


Fig. 6. Titration of a mixture of fumaric and maleic acid in pyridine with tetrabutylammonium hydroxide.

It must be pointed out, however, that the sequence in which the second acid groups are titrated is generally the reverse of that given in the foregoing example. As a rule the proton with the highest acid strength (in this case that of succinic acid) is first titrated, followed by the weaker one, just as in aqueous solutions. This is illustrated in Fig. 6. Four end-points are observed, although the first one is rather indistinct. The first equivalence point corresponds to the neutralization of the strongest acid in the mixture, *i.e.* the first proton of maleic acid. The second and third equivalence points relate to the fumaric acid and the last end-point to the weakest acid, *viz.* the second proton of the maleic acid.

The reverse sequence in the case of the first example (Fig. 5) is caused by the insolubility of the neutral tetramethylammonium oxalate in the solvent used.

Another example in which precipitate formation changes the order of titration involves the resolution of a mixture of isophthalic and terephthalic acid in a mixed solvent (Fig. 7). Three distinct end-points are obtained, the first and second corresponding to the half-neutralization and the total titration of the terephthalic acid, respectively, while the third corresponds to the total acidity of the mixture. A less distinct break between the second and the third end-point does not correspond to the half-neutralization of the isophthalic acid and attempts to improve this titration were not succesful. Moreover, the inflection observed between the first and second end-points cannot be used analytically.

When tetrabutylammonium hydroxide is used for this titration no precipitate is formed. Hence, only two end-points are obtained and resolution of these acids of approximately equal strength is impossible; the first end-point corresponds to half-neutralization of both the isophthalic and the terephthalic acid, the second to the total acidity.

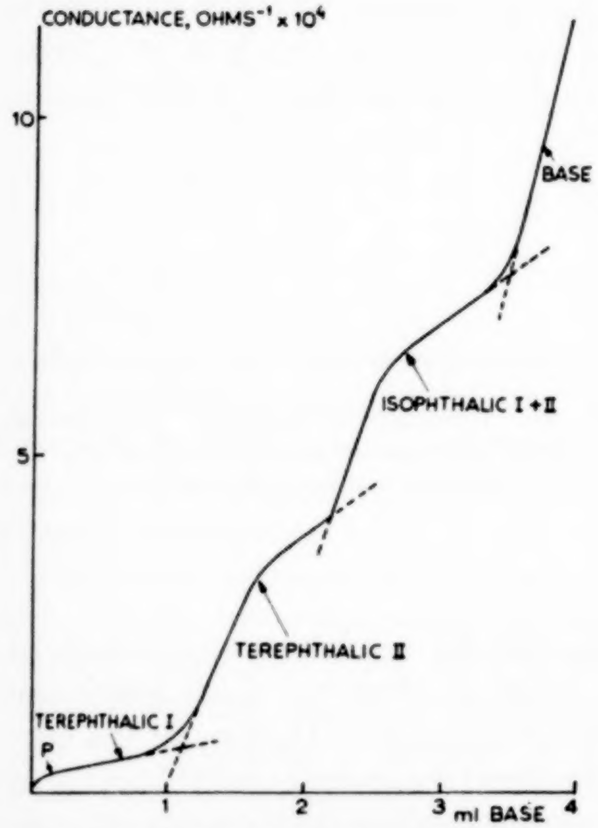


Fig. 7. Titration of a mixture of isophthalic acid and terephthalic acid in a pyridine–DMF–benzene mixture (16:4:5 v/v) with tetramethylammonium hydroxide. (p = precipitate formation)

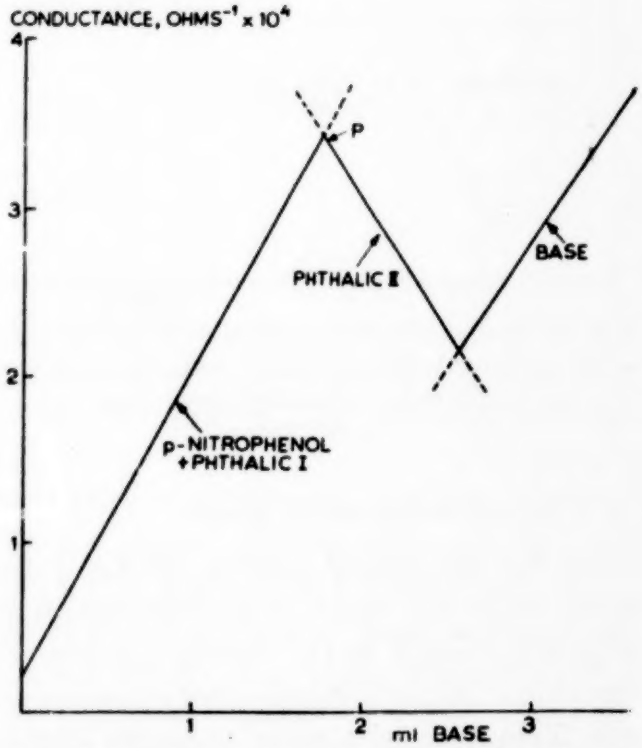


Fig. 8. Titration of a mixture of p-nitrophenol and phthalic acid in DMF with potassium methoxide. (p = precipitate formation)

2. *Binary mixtures of carboxylic and phenolic acids*

In general phenolic acids can only be titrated with potassium (sodium or lithium) methoxide, using pyridine as a solvent (*cf.* Table I in ref. 1). Hence, in the resolution of acid mixtures containing these compounds only metal bases can be used. The few carboxylic acids that can be determined with these bases in pyridine all give rise to precipitate formation. In consequence, the equivalence points in the titration curves are not usually sufficiently marked for analytical purposes.

Generally speaking, mixtures of carboxylic and phenolic acids can only be determined with sufficient accuracy by means of potentiometric titration in fairly basic solvents[6,7] or by high-frequency titration in alcoholic media[8]. Phenolic compounds which are more acidic than the alkyl phenols are an exception. Phenols with a negative substituent in the *ortho-* or *para*-position belong to this category. The determina-

References p. 455

tion of *p*-nitrophenol has been mentioned as an example. Not only pyridine but also DMF can be used as a solvent in the titration of this compound. Hence, it is possible to resolve mixtures of *p*-nitrophenol and dibasic acids which give insoluble neutral alkali salts in DMF (Fig. 8).

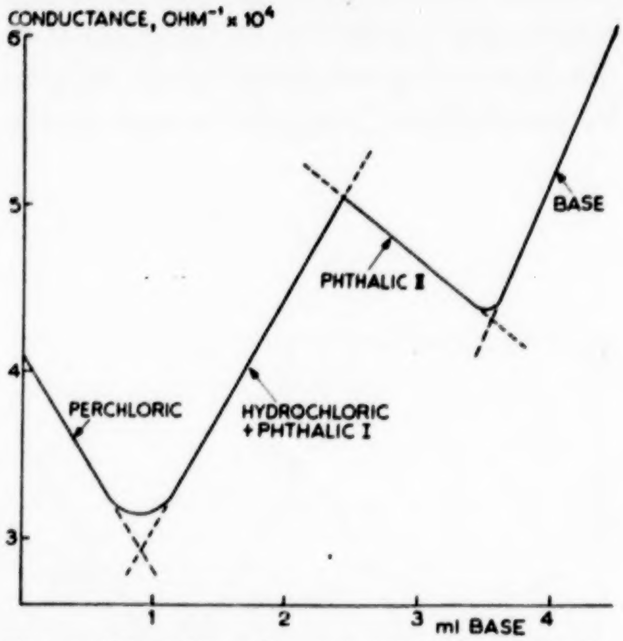


Fig. 9. Titration of a mixture of perchloric acid, hydrochloric acid and phthalic acid in pyridine with tetrabutylammonium hydroxide.

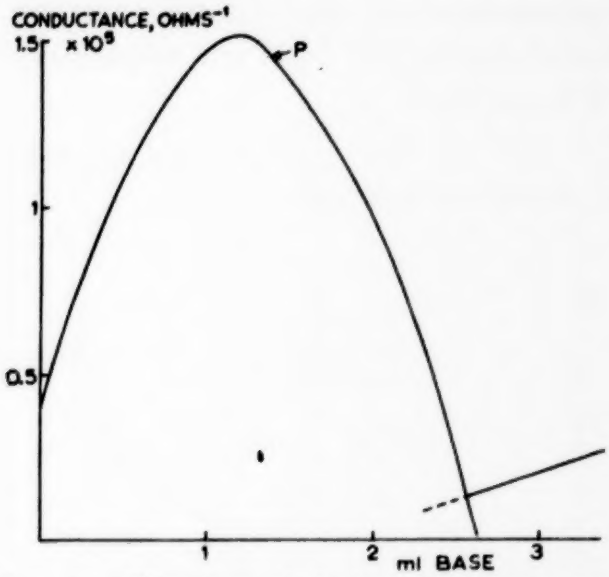


Fig. 10. Titration of diphenylolpropane in pyridine with potassium methoxide. (p = precipitate formation)

3. *Ternary mixtures of acids*

In the preceding section we have only mentioned the resolution of mixtures of acids that are weak from the conductometric point of view, *i.e.* acids which are slightly ionized in the media considered. During the titration of these acids the conductance of the solution always increases up to the (first) equivalence point because of the formation of a more strongly ionized salt. However, when strong acids are considered, *i.e.* acids which are mainly ionized, the conductance is at first fairly high; during the titration it decreases by salt formation until the equivalence point is reached and then increases normally owing to the excess of strong base. Examples of acids that are strongly ionized even in weakly basic solvents are perchloric and picric acid; sulphonic acids are of moderate strength in pyridine.

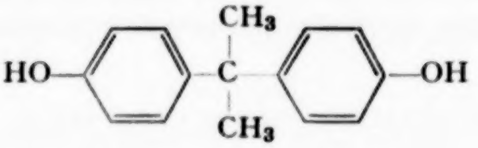
From the foregoing it is obvious that ternary acid mixtures consisting of a strong monobasic, a weak monobasic and a (weak) dibasic acid can be resolved conductometrically under suitable conditions. The result of such an analysis is shown in Fig. 9; the strongly acidic compound, perchloric acid, is neutralized during the period represented by the descending part of the curve, then the weak hydrochloric acid and one group of the phthalic acid titrated, and finally the second group of the dibasic constituent. (This procedure might be useful for the determination of the perchloric acid content of commercial-grade solutions (see under 4)).

4. *Some practical applications of non-aqueous conductometric titrations*

The conductometric titrations in non-aqueous solutions have been applied to the determination of 2 organic acids and 2 inorganic compounds. Although, strictly speaking, the latter do not belong to the class of acids studied, they have nevertheless been included because their behaviour under the particular circumstances is analogous to that of the organic acids.

a. *Diphenylolpropane.* In the first paper of this series[1] it was shown that the titration of phenolic compounds in pyridine with potassium methoxide gives satisfactory results. Both alkyl phenols and salicylic acid could be determined with a relative accuracy of 2% or better.

Recently it has been found that bivalent phenols like resorcinol can also be titrated in this way. The bipotassium salts of these compounds are insoluble in pyridine (*cf.* salicylic acid) but nevertheless a distinct equivalence point (the second one) is obtained. On this basis an analytical method has been developed for *p*-*p*-diphenylolpropane (DPP, Bisphenol A), a base material for the preparation of epoxy-resins.



The sample was dissolved in pyridine and titrated with potassium methoxide which was also dissolved in pyridine[1]. Fig. 10 shows the titration curve obtained. The solubility of the bipotassium salt of DPP in pyridine is only moderately low and the amount of precipitate thus depends strongly on the initial concentration of the phenolic compound.

The break in the curve is caused by a change from a decreasing conductance by precipitation to an increasing one by addition of excess of methoxide, so that a succesful analysis is clearly only possible when total precipitation occurs at the endpoint. When the solution is too dilute, the break in the titration curve is obtained after the stoichiometric amount of base has been added, *i.e.* when the solubility product has been exceeded (common-ion effect). But when the DPP concentration is high, methoxide may be occluded in the precipitate, again resulting in a high consumption of base. Consequently the initial DPP concentration must be chosen within certain limits. It has been found that at concentrations between 60 and 200 mg/50 ml of pyridine, the results differ less than 0.5% from the theoretical values.

Salicylic acid was used originally for the standardization of the titrant; the same limitations regarding the concentration were valid as for the DPP. The minimum amount of salicylic acid required to obtain results differing less than 0.5% from theory was 120 mg/50 ml of pyridine.

For practical purposes it is more convenient to standardize against a compound which gives no precipitate and can therefore be used in any concentration. β-Naphthol proved to be a very suitable standard. It can easily be purified by recrystallization from water (melting point 122°, corr.) and is fairly stable against oxidation by air. The titration curve of β-naphthol with potassium methoxide is given in Fig. 11 of the first paper of this series[1].

From what has been said in the preceding sections it is clear that in this determination all phenols and stronger acids interfere.

b. *Naphthenic acids.* The conductometric titration also provides a simple and fairly accurate determination of naphthenic acids in oil products. The base used is sodium or potassium methoxide in methanol–benzene (1:4 v/v). Suitable solvent mixtures are pyridine–DMF (1:1 v/v) or benzene–DMF (1:1 v/v). In the last medium a precipitate is formed but this does not interfere with the determination.

The shape of the curve is similar to that obtained for the titration of an acid of moderate strength in pyridine (*cf.* Fig. 1 in the first paper of this series[1] relating to formic acid).

c. *Perchloric acid.* The perchloric acid content of commercial solutions which contain approx. 60% of the acid can be determined conductometrically. A normal acid-base titration is not sufficient because of contamination by the decomposition product, hydrochloric acid.

The classical method for the determination of perchloric acid and perchlorates is by reduction with stannous chloride followed by back-titration of the excess with permanganate[9]. Chlorides, unless present in very low concentrations, interfere in this titration.

The conductometric determination, on the other hand, is not disturbed by hydrochloric acid, which is only weakly acidic in a pyridine solution. Moreover, it is possible to estimate the amount of hydrochloric acid present, as outlined above (see under 3). The addition of a suitable known amount of succinic acid, which can be obtained in an analytical reagent grade, allows both the standardization of the base used (tetrabutylammonium hydroxide) and the determination of the perchloric and hydrochloric acid to be done in one single titration.

The small amount of water introduced by dissolving the aqueous perchloric acid sample has little influence on the shape of the titration curve.

d. *Mixtures of inorganic acids containing sulphuric acid.* Mixtures of sulphuric acid and a (strong) monobasic inorganic acid like hydrochloric or nitric acid can be resolved in pyridine in the same way as described under 1,c for organic compounds, because these inorganic acids are only slightly ionized in weakly basic solvents.

The potentiometric titration of mixtures of strong acids containing sulphuric acid has recently been described by CUNDIFF AND MARKUNAS[5], who recommend pyridine as the most stable solvent. However HIGUCHI AND REHM[10] performed the titration of these acids conductometrically in glacial acetic acid with alkali acetates as bases. From the results given by these authors and from our findings, it would appear that for monobasic acid–sulphuric acid mixtures the conductometric or potentiometric titration in pyridine with tetrabutylammonium hydroxide is to be preferred to the one in acetic acid (the conductometric titration curve of sulphuric acid in pyridine has about the same shape as that of succinic acid[3]).

Small amounts of water do not interfere with these titrations.

CONCLUSIONS

Conductometric titrations in non-aqueous media offer many possibilities for simple and accurate differentiating determinations of acids. Single compounds as well as mixtures can be satisfactorily analyzed under suitable conditions; if these are fulfilled, conductometry can easily compete with potentiometry.

In general tetrabutylammonium hydroxide is the most versatile base, but in some special applications only alkali methoxides can be used. The most favourable solvent is pyridine, though in many cases dimethylformamide–benzene mixtures may be used instead.

Mixtures containing inorganic acids can be resolved in the same way as those with organic compounds.

ACKNOWLEDGEMENT

The authors are much indebted to Miss A. SNIP and the late Mr. P. J. LAFARGUE who skilfully carried out many of the experiments. They also wish to express their gratitude to Dr. Ir. P. N. DEGENS JR. for his stimulating interest in this investigation.

SUMMARY

A detailed study has been made of non-aqueous conductometric titrations suitable for the resolution of acid mixtures. The optimum conditions for the various determinations with respect to base and solvent are extensively discussed. The applications include determinations of diphenylolpropane, naphthenic acids, perchloric acid and mixtures containing sulphuric acid.

RÉSUMÉ

Dans le présent article les auteurs passent en revue les méthodes de titrage conductométrique de mélanges d'acides dans des solutions non-aqueuses. Ils discutent d'une façon détaillée les conditions optimales pour les différentes déterminations par rapport à la base et au solvant.

ZUSAMMENFASSUNG

Die vorliegende Arbeit gibt eine ausführliche Übersicht über Methoden zur Konduktometrischen Titration von Säuregemischen in nichtwässrigen Lösungen. Die optimalen Bedingungen für die verschiedenen Bestimmungen im Hinblick auf Base und Lösungsmittel werden eingehend besprochen.

REFERENCES

[1] N. VAN MEURS AND E. A. M. F. DAHMEN, *Anal. Chim. Acta*, 19 (1958) 64.

[2] M. ISHIDATE AND M. MASUI, *J. Pharm. Soc. Japan*, 73 (1953) 487.

[3] N. VAN MEURS AND E. A. M. F. DAHMEN, *Anal. Chim. Acta*, 21 (1959) 10.

[4] H. B. VAN DER HEIJDE, *Anal. Chim. Acta*, 17 (1957) 512.

[5] R. H. CUNDIFF AND P. C. MARKUNAS, *Anal. Chem.*, 30 (1958) 1447.

[6] J. S. FRITZ, *Acid-base titrations in nonaqueous solvents*, The G. Frederick Smith Chemical Cy, Columbus, Ohio 1952.

[7] A. H. BECKETT AND E. H. TINLEY, *Titration in non-aqueous solvents*, 2nd Ed., The British Drug Houses Ltd., Poole, England 1957.

[8] K. J. KARRMAN AND G. JOHANSSON, *Mikrochim. Acta*, (1956) 1573.

[9] I. M. KOLTHOFF AND R. BELCHER, *Volumetric Analysis*, Vol. III, Interscience Publishers, New York 1957, p. 81.

[10] T. HIGUCHI AND C. R. REHM, *Anal. Chem.*, 27 (1955) 408.

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THE SEPARATION OF HYPONITRITE FROM NITRITE, NITRATE AND HYDROXYLAMINE BY PAPER CHROMATOGRAPHY

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INTRODUCTION

Recent work in nitrate assimilation of micro-organisms has shown that nitrite, hyponitrite and hydroxylamine are likely intermediates of metabolism[1,2]. This investigation was undertaken as a preliminary to the metabolic studies, and was chiefly concerned with obtaining a separation between nitrite and hyponitrite.

The difficulty of detection of these two substances in the presence of one another is well known, and is caused mainly by the instability of hyponitrite (particularly in acid solutions), and by the fact that colours obtained with certain reagents, such as sulphanilamide-N-(1-naphthyl)ethylenediaminedihydrochloride[3] and resorcinol-periodate[4], depend upon the formation of nitrite from hyponitrite.

In this work an eluant was developed which resolved mixtures of hyponitrite with nitrite, nitrate or hydroxylamine in alkaline conditions. Under these conditions hyponitrite was stabilized during the period of elution.

EXPERIMENTAL SECTION

Preparation of sodium hyponitrite

This was carried out by a modification of the method of ADDISON *et al.*[5]. Sodium amalgam was prepared by adding small pieces of sodium metal to warm mercury in a silica crucible until the hot liquid began to solidify. The temperature of the amalgam was then raised until it was fused and a scum of molten sodium hydroxide, carbonate etc. formed on the surface. Most of this adhered to the walls of the crucible when the amalgam was agitated. The remaining bright molten metal was poured into petroleum ether and broken up into pieces in a mortar. The resulting metal amalgam (which was only slowly acted upon by water) was heated with a little distilled water to 80° under nitrogen for a short time and then washed in quick succession with cold distilled water, ethanol, acetone and petroleum ether. It was stored under petroleum ether until required for use. By this procedure a source of carbonate contamination in the sodium hyponitrite, which in the author's opinion is far more serious than aerial contamination, was eliminated.

Sodium nitrite (20 g) was dissolved in water (60 ml) and added dropwise via a tap-funnel to the purified sodium amalgam in a conical flask. Provision was made for a thermometer to dip into the reacting mixture and the bung was also fitted with entry and exit tubes for nitrogen to displace air from the flask. The temperature of the reacting mixture was kept at 60°–80° as, according to MELLOR[6], a maximum yield of hyponitrite is obtained below 100°.

The addition of sodium nitrite was stopped just before the amalgam had completely liquified, and the reaction was allowed to proceed for a further 5–10 min. The mixture was then cooled and the remaining liquid amalgam was separated. The aqueous portion was filtered rapidly by suction through a No. 541 paper and poured into a 20-fold excess of ethanol under nitrogen. After allowing this mixture to stand 1 h, the precipitated sodium hyponitrite was filtered off by suction (No. 541 paper), washed with ethanol and ether and dried in vacuo over P_2O_5 in a desiccator for 24 h. The product appeared to be of a high degree of purity because: (1) silver nitrate produced a bright yellow flocculent precipitate with a fresh solution of the salt, (2) nitrite was not detected when a concentrated solution of the salt was analyzed by paper chromatography (see below), (3) the material was shown to be free from carbonate by boiling it with water for a few minutes to destroy $N_2O_2^{-2}$ followed by the addition of a few drops of fresh baryta solution. No turbidity was observed.

The compound, when dry, could be kept indefinitely in a stoppered container.

Paper chromatography of hyponitrite-containing mixtures

Freshly prepared solutions of sodium hyponitrite in 2 N NaOH were mixed with sodium nitrite, nitrate, or a solution of hydroxylamine sulphate in sodium hydroxide. Resolution of the mixtures was effected by downward chromatography on acid washed Whatman No. 1 paper strips in an eluant containing: ethanol 70 ml, water 30 ml, sodium hydroxide 2 g. During elution the eluant was frontally analyzed on the chromatogram. Hyponitrite was contained within the upper sodium hydroxide zone, while nitrite, nitrate and hydroxylamine moved with the ethanol–water zone further down the chromatogram. Approximate R_F values were: 0.1 for $N_2O_2^{-2}$ and 0.5–0.6 for NO_2^-, NO_3^- and NH_2OH. Hyponitrite and nitrite were developed by using a modification of VEPŘEK-SIŠKA's reagent[4]. Equal volumes of solutions of resorcinol in glacial acetic acid and sodium meta-periodate in water were mixed as required and sprayed on to the dried chromatogram. Brown spots were obtained which gave an orange fluorescence in U.V. light, and which darkened on standing, or by exposing them to ammonia. 1 μg of $N_2O_2^{-2}$ was easily detected on the chromatogram by fluorescence in U.V. light after the resorcinol-periodate treatment, and 1 μg of NO_2^- was seen in daylight after the same treatment.

When sodium hydroxide was replaced by ammonia in the eluant, double spotting was observed with nitrite, due, presumably, to competition between sodium and ammonia for the anion.

Nitrate was not detected by the resorcinol-periodate reagent but appeared as a fluorescent spot in U.V. light after dipping the chromatogram in an ethereal solution of 8-hydroxyquinoline (oxine) or spraying the paper with a solution of nitron in 60% acetone followed by exposure of the dried chromatogram to ammonia. The nitron test was a modification of the method used by POLLARD[7] for detecting nitrate. Nitrite did not fluoresce with nitron but did so with oxine in U.V. light. Nitrite and nitrate presumably move as the sodium salts as sodium was present in the excised spots, whereas other portions of the chromatogram (with the exception of the frontally-analyzed NaOH band) were free from this metal.

Hydroxylamine was detected by spraying the damp chromatograms with either the resorcinol-periodate reagent (orange–brown band) or alkaline copper citrate solution (brownish yellow band on a blue background). The latter reagent was prepared as required by mixing solutions of cupric chloride and citric acid and adding sodium hydroxide until a precipitate began to form in the dark blue liquid. If the chromatogram was dried completely, no hydroxylamine could be detected owing, presumably, to its volatilization from the paper.

The chromatographic method was found to be useful for testing the purity of hyponitrite material prepared from other sources. Samples of silver hyponitrite, which had been made by the interaction of hydroxylamine sulphate and sodium nitrite and precipitated with silver nitrate, were analysed by decomposing them with a few drops of a saturated solution of sodium chloride and stabilizing the liberated $N_2O_2^{-2}$ with 1–2 drops of 12 N NaOH. After filtering, spots of the solution were analysed on paper strips, and the results showed that even when the silver compound had been thoroughly washed with water until the washings ceased to give a definite NO_2^- reaction with the sulphanilamide-naphthyl reagent[3], traces of NO_2^- could be detected on the paper strip. This, presumably, was due to the adsorption of NO_2^- ions by silver hyponitrite during the precipitation.

All samples of sodium hyponitrite gave, on chromatograms developed with the resorcinol-periodate reagent, a weak brown spot of unknown origin at R_F 0.8–0.9. The phenomenon also occurred when spots of the strongly alkaline solution obtained after amalgam reduction of the nitrite were run on paper strips, but the spot was weaker than that obtained from samples of precipitated sodium hyponitrite. The substance responsible for this phenomenon must therefore be co-precipitated with sodium hyponitrite when the amalgam reduced solution is poured into an excess of ethanol. Impurities in the starting materials were ruled out because the spot was not obtained when concentrated solutions of $NaNO_2$ or sodium amalgam in water were run separately on paper strips.

The R_F value of this spot, and its stability in this region precludes it from being due to $N_2O_2^{-2}$ or NH_2OH; failure to give a colour with the sulphanilamide-naphthyl reagent unless $NaIO_4$ solution was added suggests that it is not due to NO_2^-, but is oxidized to the latter by the periodate. Hydrazine and (sodium) azide were also ruled out because their behaviour on paper chromatograms was not compatible with that of the uncharacterized substance (R_F values: NaN_3 0.62, N_2H_4 streaks to 0.5).

Sodium hyponitrite (200 mg) was dissolved in a minimum of 2 N NaOH, and the solution placed on a column of dry cellulose. Elution was carried out with the ethanol–water–sodium hydroxide eluant and the first few milliliters of eluant at breakthrough were found by chromatographic analysis to contain a concentration of the uncharacterized material. When this eluant was evaporated over P_2O_5 in vacuo, analysis by paper strip chromatography showed that only NO_2^- was present in the residue.

These observations suggest that the material is a reduction product of NO_2^- which is converted back to the latter by aerial oxidation.

SUMMARY

The preparation of carbonate-free sodium hyponitrite and the resolution by paper chromatography of mixtures of sodium hyponitrite with sodium nitrite, nitrate, or hydroxylamine are

described. Observations were made upon an uncharacterized impurity which was present in very small amounts in the prepared sodium hyponitrite samples.

RÉSUMÉ

L'auteur décrit la préparation d'un hyponitrite de sodium, exempt de carbonate et la séparation de cet hyponitrite d'avec nitrite, nitrate et hydroxylamine, par chromatographie sur papier.

ZUSAMMENFASSUNG

Es wird die Darstellung eines carbonat-freien Natriumhyponitrits sowie die papierchromatographische Trennung von Gemischen von Natriumhyponitrit, Natriumnitrit, Natriumnitrat und Hydroxylamin beschrieben.

REFERENCES

[1] A. Medina and D. J. D. Nicholas, *Biochim. Biophys. Acta*, 25 (1957) 138.

[2] D. J. D. Nicholas, 13th Symp. of Soc. Exp. Biol. on "*Utilization of Nitrogen and its Compounds by Plants*", Cambridge Univ. Press, 1959, p. 1.

[3] F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, D. Van Nostrand Co. Inc., New York 1953, p. 422.

[4] J. Vepřek-Siška, V. Pliška and F. Smirous, *Analyst*, 84 (1959) 119.

[5] C. C. Addison, G. A. Gamlen and R. Thompson, *J. Chem. Soc.*, (1952) 338.

[6] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. VIII, Longmans, Green and Co, Ltd., London 1928, p. 404.

[7] F. H. Pollard, private communication.

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GRAVIMETRIC DETERMINATION OF COBALT AND NICKEL, AND THEIR SEPARATIONS FROM COPPER WITH N-BENZOYLPHENYLHYDROXYLAMINE

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N-benzoylphenylhydroxylamine was suggested by Shome[1] as a reagent for the analysis of many metals and has been used for the gravimetric determination of copper, iron, aluminium and titanium[2], and for the colorimetric estimation of vanadium[3]. In the present investigation cobalt and nickel are precipitated separately with this reagent from their hot buffered solutions. The metal complexes correspond to the formulae $Co(C_{13}H_{10}O_2N)_2$ and $Ni(C_{13}H_{10}O_2N)_2$, and can be weighed directly. By adjusting the pH of the solutions it is possible to separate either cobalt or nickel from copper and to determine the component metals of any of the mixtures.

SOLUTIONS USED IN THE DETERMINATION OF THE METALS

Metals to be determined

Separate standard solutions of cobalt sulphate, nickel ammonium sulphate and copper sulphate were prepared to contain 1.05 mg of cobalt, 1.22 mg of nickel and 1.32 mg of copper respectively per ml.

All the chemicals used were of A.R. quality.

DETERMINATION OF COBALT AND NICKEL

A known quantity of the cobalt or nickel solution (20 to 30 ml) was diluted to 300 ml with distilled water and heated to boiling. (In the case of cobalt, 10 ml of a 2 % hydroxylamine hydrochloride solution were added to prevent subsequent formation of any cobaltic complex.) Benzoylphenylhydroxylamine (0.25 to 0.3 g) solution in alcohol (10 to 15 ml) was slowly added to the hot solution of the metal. A 10 % sodium acetate solution (5 to 10 ml) was added to maintain the pH of the solution between 5.5 and 6.5, estimated with pH paper. The mixture was stirred occasionally during one hour on a boiling water-bath. The precipitate was then filtered, washed, and ignited to the oxide. The cobalt oxide was heated with a mixture of concentrated nitric and sulphuric acids and weighed as cobalt sulphate; the nickel was weighed as nickelous oxide.

The results (Table I) indicate that cobalt and nickel ions are quantitatively precipitated with benzoylphenylhydroxylamine and can be weighed as cobalt sulphate and nickel oxide respectively.

TABLE I

DETERMINATION OF NICKEL OR COBALT BY WEIGHING AS NICKEL OXIDE OR COBALT SULPHATE

Metal taken (g)	*Weight of ppt. (g)*	*Metal found (g)*	*Error (g)*
Co		Co	
0.02623	0.06860	0.02610	— 0.00013
0.03147	0.08230	0.03130	— 0.00017
0.02518	0.06650	0.02530	+ 0.00012
0.02413	0.06310	0.02400	— 0.00013
Ni		Ni	
0.06086	0.07700	0.06050	— 0.00036
0.05852	0.07460	0.05861	+ 0.00009
0.05628	0.07180	0.05641	+ 0.00013
0.05384	0.06880	0.05406	+ 0.00022
0.04856	0.06160	0.04841	— 0.00015

pH of solution = 5.5 to 6.5.

TABLE II

DETERMINATION OF COBALT AND NICKEL BY WEIGHING THE METAL COMPLEXES DIRECTLY

Metal taken (g)	*Weight of ppt. (g)*	*Metal found (g)*	*Error (g)*
Co			
0.03147	0.25710	0.03139	— 0.00008
0.02938	0.24110	0.02943	+ 0.00005
0.02833	0.23290	0.02834	+ 0.00001
0.02729	0.22220	0.02713	— 0.00016
0.02623	0.21600	0.02637	+ 0.00014
Ni			
0.03048	0.24920	0.03030	— 0.00018
0.02926	0.24180	0.02941	+ 0.00015
0.02804	0.23160	0.02816	+ 0.00012
0.02682	0.21980	0.02672	— 0.00010
0.02438	0.20150	0.02450	+ 0.00012

In another series of experiments, cobalt and nickel were precipitated separately with benzoylphenylhydroxylamine as described above. The precipitate was then filtered on a No. 3 sintered glass crucible, washed well with hot water and dried at 110–120° to constant weight. The metal contents were calculated on the basis that the precipitates contained 12.21% of cobalt and 12.16% nickel respectively.

It can be seen from Table II that the precipitates of cobalt and nickel with benzoylphenylhydroxylamine can be determined by weighing the precipitates directly. At pH values above 6.5, the precipitates form hard lumps (and in the case of nickel the solution also becomes coloured) whereas below pH 5.5 the precipitation of the metals is incomplete. If the cobalt is precipitated without prior addition of hydroxylamine hydrochloride the results obtained are slightly high, probably owing to the formation of a small amount of cobaltic complex in the precipitate.

GRAVIMETRIC SEPARATIONS OF COBALT AND NICKEL FROM COPPER

A mixture containing known amounts of copper sulphate and either cobalt sulphate or nickel ammonium sulphate was diluted to 400 ml with distilled water. Sulphuric acid (4 to 5 ml of 1.5 *N*) and 10% sodium acetate solution (15 ml) were then added to adjust the pH to about 4.0. The solution was heated to boiling and copper was precipitated by the gradual addition of benzoylphenylhydroxylamine (0.25 to 0.35 g) dissolved in alcohol (5 to 10 ml). The copper precipitate was heated on the water-bath for one hour with occasional stirring, filtered on a No. 3 sintered glass-crucible, washed well (the wash-water contained sufficient sodium acetate and sulphuric acid in distilled water to maintain the pH at about 4.0), and dried at 110°–120° to constant weight. The copper content of the precipitate was calculated on the basis that the precipitate contained 13.03% of copper.

The filtrate and washings were evaporated to about 300 ml and filtered. During

TABLE III

SEPARATION OF COBALT FROM COPPER

Mixture No.	*Metal taken (g)*		*Wt. of ppt. (g)*		*Metal found (g)*		*Error (g)*	
	Cu	*Co*	*Cu*	*Co*	*Cu*	*Co*	*Cu*	*Co*
1	0.03311	0.02623	0.25329	0.21550	0.03296	0.02631	−0.00015	+0.00008
2	0.03973	0.03147	0.30600	0.25800	0.03987	0.03150	+0.00014	+0.00003
3	0.02781	0.02833	0.21180	0.23250	0.02760	0.02839	−0.00021	+0.00006
4	0.03046	0.02938	0.23480	0.23400	0.03060	0.02930	+0.00014	−0.00008
5	0.02649	0.02623	0.20500	0.21320	0.02679	0.02603	+0.00030	−0.00020

TABLE IV

SEPARATION OF NICKEL FROM COPPER

Mixture No.	*Metal taken (g)*		*Wt. of ppt. (g)*		*Metal found (g)*		*Error (g)*	
	Cu	*Ni*	*Cu*	*Ni*	*Cu*	*Ni*	*Cu*	*Ni*
1	0.03973	0.03048	0.30590	0.25160	0.03985	0.03051	+0.00012	+0.00003
2	0.03311	0.02926	0.25480	0.24020	0.03320	0.02914	+0.00009	−0.00012
3	0.03046	0.02682	0.23200	0.22180	0.03036	0.02690	−0.00010	+0.00008
4	0.02781	0.02804	0.21510	0.22960	0.02801	0.02786	+0.00020	−0.00018
5	0.02649	0.02438	0.20250	0.20110	0.02638	0.02440	−0.00011	+0.00002

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the concentration of the filtrate an organic precipitate appeared in the solution, probably owing to the prolonged heating of the reagent solution in air. Before the subsequent determination of cobalt, 20 ml of 2% hydroxylamine hydrochloride solution were added. Cobalt or nickel in the solution was then determined as described above.

The results in Tables III and IV indicate that cobalt or nickel can be separated from copper and the two component metals of the mixtures can be determined separately.

CONCLUSIONS

Cobalt and nickel can be determined with N-benzoylphenylhydroxylamine, the precipitates being directly weighable. For the determination of cobalt the present method offers the advantage over the α-nitroso-β-naphthol method that the precipitate need not be ignited and converted to cobalt sulphate. By the methods described, cobalt or nickel can be separated from copper and the individual metals determined by direct weighing. The procedure is simple and the organic reagent can be prepared easily and stored indefinitely.

ACKNOWLEDGEMENT

One of the authors (S. K. Sinha) is indebted to the Ministry of Scientific Research and Cultural Affairs, Government of India for the grant of a scholarship.

SUMMARY

N-Benzoylphenylhydroxylamine can be used for the gravimetric determination of cobalt and nickel. The precipitates can be weighed as such, or ignited and weighed as cobalt sulphate or nickelous oxide. Cobalt or nickel can be separated from copper with the reagent.

RÉSUMÉ

La N-benzoylphénylhydroxylamine est proposée comme réactif pour le dosage gravimétrique du cobalt et du nickel. Ces deux cations sont précipités séparément et peuvent être séparés d'avec le cuivre.

ZUSAMMENFASSUNG

Kobalt und Nickel können mit Hilfe von N-Benzoylphenylhydroxylamin gravimetrisch bestimmt werden. Die beiden Metalle können einzeln gefällt und gleichzeitig von Kupfer abgetrennt werden.

REFERENCES

[1] S. C. Shome, *Current Sci.*, India, 13 (1944) 257.
[2] S. C. Shome, *Analyst*, 75 (1950) 27.
[3] S. C. Shome, *Anal. Chem.*, 23 (1951) 1186.

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DETERMINATION OF ARSENIC IN ORGANIC COMPOUNDS

RAPID MICRO AND SEMIMICRO METHODS

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The extension of his rapid method for the micro determination of halogens and sulfur in organic compounds[1] to the determination of phosphorus, arsenic and metals was predicted by SCHÖNIGER[2]. In this method, the sample is wrapped in a filter paper envelope, affixed to the end of a platinum wire, and burned in an oxygen-filled flask containing a suitable liquid absorbent for the desired products of combustion. This method has been successfully applied to the determination of phosphorus[3] and mercury[4]. In attempting to extend this method to the determination of arsenic, variable, but consistently low results were obtained. Because the platinum support was pitted, arsenic was presumed to be lost by reaction with the platinum. Replacement of the platinum with a quartz spiral was not satisfactory because the quartz devitrified during the course of a single combustion.

In 1952, ZAK *et al.* prepared 28% chloric acid and used it for the determination of iodinated organic compounds[5] and for the digestion of organic matter in the determination of serum protein-bound iodine[6,7]. Improvements in the technique for serum protein-bound iodine were made by several investigators[8-10]. MCCHESNEY AND HOPPE[11] have adapted this method to the determination of iodine containing radiopaques in tissues. MCCHESNEY AND BANKS[12] used digestion with chloric acid in their determination of sulfur in biological materials.

Because chloric acid oxidizes organic matter smoothly and rapidly at about 180°, it is to be preferred to the more widely used sulfuric acid or sulfuric–nitric acid digestions or alkaline fusions. Excess acid is easily boiled off to leave a perchloric acid solution of the inorganic elements, usually present in one of their higher oxidation states.

APPARATUS AND REAGENTS

Most of the apparatus and reagents used are common laboratory items. The following special solutions are needed.

Chloric acid, 28%. Prepared by the method of ZAK[7] or of STRICKLAND AND MALONEY[10] if the reagents used in the preparation are of unknown purity.

Standard 0.005 *N trivalent arsenic*. Transfer 247.3 mg of reagent grade arsenic trioxide, previously dried to constant weight at 105°, to a 1000-ml volumetric flask.

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Dissolve the solid in 4 ml of 1 *N* sodium hydroxide, neutralize the solution to phenolphthalein indicator by dropwise addition of 6 *N* hydrochloric acid, then add 50 g of sodium bicarbonate. Dilute to 1000 ml with distilled water, mix well.

Standardized 0.005 *N iodine.* Dissolve 2 g of sodium iodide in 5 ml of distilled water, add 0.65 g of iodine, and agitate until the iodine is dissolved. Dilute to 1000 ml with distilled water, mix well. Standardize by titration against the standard trivalent arsenic solution, using starch indicator.

Colorimetric reagent. Mix equal volumes of 2.5% (w/v) ammonium molybdate in water and 1% (w/v) bismuth subcarbonate U.S.P. in 7 *N* sulfuric acid. Immediately before use add 10 g of ascorbic acid per 100 ml of solution. Use of this reagent as directed below will give the optimum acidity for color development. This method is a modification of the procedure suggested by JEAN[13].

Standard arsenic solution. Digest arsenic trioxide or an organic arsenical of known purity with chloric acid as set forth below. Dilute the neutralized digest to produce a solution containing about 10 μg of arsenic per ml.

DIGESTION WITH CHLORIC ACID

The following digestion is used for both the micro and semimicro determination. Transfer a weighed sample containing 4 to 5 mg of arsenic to a 250-ml glass-stoppered conical flask for the semimicro method, or, transfer a weighed sample containing 0.25 to 0.6 mg of arsenic to a 250-ml conical flask for the micro method. Add 10 ml of chloric acid and digest on a hot plate until heavy white fumes of perchloric acid are produced and the solution is colorless. Do not allow the digest to evaporate to dryness. Remove the flask from the hot plate, cool, add 2 ml of distilled water, 1 drop of phenolphthalein indicator, and neutralize with 10% sodium hydroxide solution (about 5 ml required). Discharge the phenolphthalein color by dropwise addition of 6 *N* hydrochloric acid.

For the digestion of larger amounts of organic matter, 35 ml of chloric acid per gram of sample has been found adequate, but in no case should less than 10 ml of chloric acid be used.

SEMIMICRO METHOD

Procedure

To the neutralized digest add 25 ml of 1 *N* hydrochloric acid, then 1 g of sodium iodide. Stopper the flask, swirl to dissolve the iodide, loosen the stopper, heat on a steambath for 15 min, then cool to room temperature. Discharge the iodine color by titration with approximately 0.005 *N* sodium thiosulfate solution, adding 2 ml of starch indicator toward the end of the titration. Add sodium bicarbonate in small portions to neutralize the acid, then saturate the solution with bicarbonate as shown by the presence of undissolved bicarbonate. Titrate with recently standardized 0.005 *N* iodine solution. Arsenic which has been reduced to the trivalent state by hydriodic acid is quantitatively re-oxidized by iodine to the pentavalent state. The conditions were recommended by FLEURY[14] in his critical review.

Accuracy and reproducibility

Ten samples of *p*-arsanilic acid (theoretical arsenic content 34.5%), ranging from 6.8 to 13.2 mg in weight, were assayed with the following results in per cent arsenic:

34.5, 34.5, 34.3, 34.8, 34.8, 34.7, 34.8, 34.3, 34.6, 34.5; average: 34.6. By the method given by DEAN AND DIXON[15] the 99% confidence interval is ± 0.2 which gives a 99% confidence level for this method of 6 parts per thousand.

Assays of four samples of *o*-arsanilic acid (theoretical arsenic content 34.5%) ranging from 9.3 to 11.0 mg in weight gave the following results in per cent arsenic: 33.7, 33.5, 33.6, 33.9; average: 33.7. The 99% confidence interval is ± 0.5 or 15 parts per thousand.

Analyses of other arsenicals are shown in Table I. These samples had been prepared as research compounds at the Sterling-Winthrop Research Institute and may be considered to be at least 97% pure based on elemental analyses for carbon, hydrogen, and nitrogen.

TABLE I

ASSAYS BY SEMIMICRO METHOD

Substance	*Sample weight mg*	% *As found*	% *As theory*	% *error*
3-2 (hydroxethylureido)-4-hydroxy phenylarsonic acid	21.106	23.46	23.40	+0.3
6,7-dimethoxy-3-nitro-9-(3-diethyl amino-2-hydroxypropylamine-acridine di-(4-glycoly-aminophenylarsonate) (Rutenol^{R})	30.182	15.61	15.31	+2.0
Sodium p-N-glycolylarsanilate tetrahydrate (Quarcy^{R})	11.221	20.74	20.30	+2.2
4-(2-hydroxyethylureido)-phenylarsonic acid	22.783	24.65	24.63	+0.1
0.1 *N* sodium arsenite solution	1.00 ml	0.373	0.375	—0.5

Application to commercial preparation

A 750-mg sample of a 7-g suppository which was claimed to contain 250 mg of acetarsone in a glycerinated gelatin base was assayed by the above procedure. Recovery was 103% of claim.

Interference

Five ml of conc. hydrochloric acid were added to a sample of *p*-arsanilic acid before digestion to give a calculated initial chloride concentration of about 4 *M*. Recovery of arsenic was 99.6%.

Because the presence of bismuth in glycobiarsol, U.S.P. (Milibis^{R}) gives a yellow bismuth iodide complex which interferes in the titration with thiosulfate, the procedure was modified by the following addition. After reduction of the arsenic with hydriodic acid, 10 ml of a 0.1 *M* solution of disodium (ethylene dinitrilo) tetra-acetate were added, and the solution cautiously adjusted to about pH 2 with sodium carbonate in order to discharge the color of the bismuth iodide complex. It had been previously determined that this procedure did not affect the titration of trivalent arsenic with iodine. Despite this change, the method gave results for arsenic of only 20 to 35% of the expected value. It was thought that bismuth might interfere in the reduction of pentavalent arsenic by lowering the effective concentration of iodide, but replacement of the hydrochloric acid and sodium iodide with 1 *N* hydriodic acid was without effect. It is postulated that a bismuth–arsenic–iodide complex is formed which is not as readily reduced by hydriodic acid to arsenic (III) as arsenic(V) iodide.

MICRO METHOD

Procedure

Dilute the neutralized digest to 100 ml in a volumetric flask. In test tubes graduated at 10 ml introduce 2-ml aliquots of the standard arsenic solution, the sample dilution, and distilled water. Dilute each to 7 ml. To each add 2 ml of the colorimetric reagent, dilute to 10 ml, mix the contents of each tube, and allow to stand for 5 min. Read the absorbance in a suitable colorimeter using a filter having a maximum transmittance at 660 mμ, setting the instrument to zero absorbance with the distilled water blank. The color is stable for at least 1 h. The color produced follows the Beer-Lambert law at least up to 40 μg of arsenic in the final 10-ml volume.

TABLE II

ASSAYS BY MICRO METHOD

Substance	*Sample weight mg*	*Absorbance*	*% As found*	*% error*
Glycobiarsol, U.S.P.-14.78% As, (Milibis^{R})	5.605	0.253	14.7	—0.6
o-Arsanilic acid-33.7% As	4.860	0.495	33.3	—1.2
	4.205	0.423	32.8	—2.7
	2.224	0.235	34.5	+2.4
4-(2-Hydroxyethylureido)-phenylarsonic acid-24.6% As	2.897	0.221	25.9	+5.3
	2.395	0.186	25.4	+3.3
	2.346	0.180	25.0	+1.6
	2.446	0.186	24.8	+0.8
	2.421	0.186	25.1	+2.0

Reproducibility and accuracy

Seven samples of *p*-arsanilic acid, ranging from 1.6 to 4.0 mg in weight, were run, as described above, on different days. The absorbance per mg of arsenic in 10 ml of final dilution measured in a particular set of cells in our colorimeter were: 15.8, 15.1, 15.4, 15.0, 15.4, 15.3, 15.2; average: 15.3. The 99% confidence interval is ± 0.4 or 26 parts per thousand.

Using the average absorbance per mg of arsenic found for *p*-arsanilic acid, samples of 4-(2-hydroxyethylureido)-phenylarsonic acid found to contain the theoretical 24.6% of arsenic by the semimicro method were assayed by the micro method. Results are shown in Table II. Other compounds not containing their theoretical amount of arsenic are also shown in Table II. It is interesting to note that the sample of Milibis^{R}, which could not be assayed by the semimicro method, gave excellent results by the micro method.

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Interference

Phosphorus interferes by formation of a heteropoly blue similar to that formed by pentavalent arsenic. Phosphorus and arsenic, if present together, may be separated and determined, after digestion of the sample with chloric acid, by the method given by JEAN[13].

SUMMARY

Rapid micro and semimicro methods for determination of arsenic in organic compounds have been developed using 28% chloric acid as the digesting agent for the organic arsenical. This wet acid digestion procedure does not lead to loss of arsenic even in the presence of 4 M chloride. The semimicro method completes the assay by reduction of the pentavalent arsenic with iodide, destruction of the iodine liberated with thiosulfate and re-oxidation to pentavalent arsenic with iodine in a buffered solution. The micro method completes the assay by development of a heteropoly molybdenum blue using a single solution reagent at room temperature. The color is reproducible so that only a single calibration curve for the instrument used is necessary.

RÉSUMÉ

Les auteurs proposent une méthode semimicrochimique et une méthode microchimique pour le dosage de l'arsenic dans des matières organiques. La substance à analyser est attaquée par l'acide chlorique. Le dosage semimicrochimique consiste à réduire l'arsenic (V) par un iodure et à titrer ensuite l'arsenic(III) formé par l'iode. Dans le procédé microchimique, on procède par colorimétrie du bleu de molybdène.

ZUSAMMENFASSUNG

Es wird eine mikro- und halbmikrochemische Methode zur Bestimmung von Arsen in organischen Substanzen beschrieben. Der Aufschluss der Substanz erfolgt mit Chlorsäure. Bei der Halbmikromethode wird das gebildete Arsen(V) zu Arsen(III) reduziert und dieses mit Jodlösung titriert. ei der Mikromethode erfolgt die Bestimmung kolorimetrisch nach Bildung von Molybdänblau.

REFERENCES

[1] W. SCHÖNIGER, *Mikrochim. Acta.*, (1955) 123; (1956) 869.
[2] W. SCHÖNIGER, *Midatlantic Analytical Symposium*, Philadelphia, Pa., Feb. 8, 1957.
[3] K. D. FLEISCHER, B. C. SOUTHWORTH, J. H. HODECKER AND M. M. TUCKERMAN, *Anal. Chem.*, 30 (1958) 152.
[4] B. C. SOUTHWORTH, J. H. HODECKER AND K. D. FLEISCHER, *Anal. Chem.*, 30 (1958) 1152.
[5] B. ZAK AND A. J. BOYLE, *J. Am. Pharm. Assoc., Sci. Ed.*, 41 (1952) 260.
[6] B. ZAK, A. M. KOEN AND A. J. BOYLE, *Am. J. Clin. Pathol.*, 23 (1953) 603.
[7] B. ZAK, H. H. WILLARD, G. B. MEYERS AND A. J. BOYLE, *Anal. Chem.*, 24 (1954) 1345.
[8] J. F. GOODWIN, R. B. HAHN AND A. J. BOYLE, *Anal. Chem.*, 29 (1957) 1681.
[9] H. H. LEFLER, *Am. J. Clin. Pathol.*, 24 (1954) 483.
[10] R. D. STRICKLAND AND C. M. MALONEY, *Anal. Chem.*, 29 (1957) 1870.
[11] E. W. MCCHESNEY AND J. O. HOPPE, *Am. J. Roentgenol. Radium Therapy Nuclear Med.*, 78 (1957) 137; *Arch. intern. pharmacodynamie*, 99 (1954) 127.
[12] E. W. MCCHESNEY AND W. F. BANKS, JR., *Anal. Chem.*, 27 (1955) 987.
[13] M. JEAN, *Anal. Chim. Acta*, 14 (1956) 172.
[14] P. FLEURY, *J. Pharm. Chim.*, 21 (1920) 385.
[15] R. B. DEAN AND W. J. DIXON, *Anal. Chem.*, 23 (1951) 636.

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COULOMETRIC-ACIDIMETRIC TITRATIONS IN ANHYDROUS ACETIC ACID*

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As pointed out by LINGANE[1], the extension of coulometric methods to non-aqueous solvents would greatly broaden the practical scope of the technique. However, only a handful of coulometric experiments involving non-aqueous media have been reported. MEYER AND BOYD[2] have described a method for a coulometric Karl Fischer titration in a methanol solution. STREULI[3] and HANSELMAN AND STREULI[4] described a coulometric titration of several amines in acetonitrile. In the latter case the supporting electrolyte was 0.05 *F* lithium perchlorate trihydrate, and the three waters of hydration provided enough water so that its oxidation to oxygen served as the hydrogen ion-producing electrode reaction. HANSELMAN AND STREULI[4] have also used the oxidation of hydroquinone to quinone in acetonitrile to generate hydrogen ion.

The large number of volumetric-acidimetric titrations[5] which have been described in which acetic acid is used as the solvent led us to try to develop a coulometric titration procedure for this solvent in order to make the titration as catholic as possible. The procedure which has resulted combines the advantages of both coulometric and non-aqueous acidimetric titrations. It should be applicable to the determination of μg-quantities of bases which are too weak to be titratable with acid in aqueous solutions.

The generation of hydrogen ion in anhydrous acetic acid-acetic anhydride mixtures was accomplished by anodically oxidizing a mercury electrode. The predominant electrode reaction which occurs is reaction (1):

$$2Hg + 2CH_3COOH = Hg_2(CH_3COO)_{2(s)} + 2H^+ + 2e^- \quad \ldots\ldots\ldots \quad (1)$$

The generation of hydrogen ions proceeds with 100% current efficiency in a supporting electrolyte of sodium perchlorate. The mercury(I) acetate which is formed is a stable, insoluble precipitate which accumulates during the titration.

EXPERIMENTAL

Except for the sodium perchlorate all chemicals used were commercial products of highest purity and were used without further purification.

All batches of sodium perchlorate which were tested by us contained significant amounts of basic impurities which had very deleterious effects on the sharpness of the potentiometric end-point. After one recrystallization from hot acetic acid the impurities were reduced to an acceptably low level and the end-point sharpness was substantially improved.

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* Contribution No. 2470 from the Gates and Crellin Laboratories of Chemistry.

Hydrogen ions were generated in a supporting electrolyte prepared by dissolving 0.1 formula weight of sodium perchlorate in a solvent consisting of one part (by volume) acetic acid to six parts acetic anhydride.

Standard solutions of base were prepared by dissolving weighed quantities of sodium carbonate or potassium hydrogen phthalate in measured volumes of acetic acid.

The titration cell consisted of a 150-ml beaker fitted with a rubber stopper. The solution in the cell was stirred magnetically. Although the solvent gradually attacked the rubber stopper, no impurities appeared to be introduced into the solution during the time required for a titration (up to 45 min). The mercury-generating anode employed was either a 5-cm^2 amalgamated gold electrode or a mercury pool electrode of approximately 20 cm^2. Both electrodes functioned well, but the large pool electrode was more suitable for titrations of larger amounts of base because the resulting mercury(I) acetate did not tend to insulate this electrode from the solution. The auxiliary cathode consisted of a platinum wire separated from the body of the solution by a sintered glass tube. The cathode compartment was filled with the same supporting electrolyte as the anode compartment. Hydrogen gas was evolved at the cathode.

The titration was followed potentiometrically by means of a glass electrode and a specially constructed mercury–mercurous acetate reference electrode. The glass electrode was stored in acetic acid when not in use in order to maintain its sensitivity; storage in water or acetic anhydride caused the reproducibility and sensitivity of the electrode to decrease markedly.

An ordinary calomel reference electrode could not be employed not only because chloride ion is titrated as a base in the solvent used, but also because the sodium perchlorate supporting electrolyte causes potassium perchlorate to precipitate at the junction of the calomel reference electrode and spurious potential readings result. The mercury–mercurous acetate reference electrode was prepared by adding excesses of solid mercurous acetate and mercury metal to anhydrous acetic acid, which was saturated with sodium perchlorate. Connection with the solution was accomplished by means of a sodium perchlorate salt bridge.

The potential of the glass-reference electrode pair was measured with the mV-scale of a Leeds and Northrup pH Indicator. The potentials measured had no absolute significance but could be used empirically to detect the end-point of the titration.

The constant current source was modeled after that described by LINGANE[6]. Even though the resistance of the supporting electrolyte was from 2000 to 6000 Ohms, currents from 1–25 mA were maintained constant to ± 0.05%.

THE TITRATION

Hydrogen ion generation current efficiency

The oxidation of a mercury electrode in anhydrous acetic acid is a very satisfactory means of generating hydrogen ion with 100% current efficiency. This is true because the predominant electrode reaction, (1), as well as the most likely side reactions, (2), (3), and (4), all correspond to 100% current efficiency for generation of hydrogen ion:

$$Hg + 2CH_3COOH = Hg(CH_3COO)_2 + 2H^+ + 2e^- \quad (2)$$

$$2CH_3COOH = (CH_3CO)_2O + \tfrac{1}{2}O_2 + 2H^+ + 2e^- \quad (3)$$

$$2CH_3COOH = C_2H_6 + 2CO_2 + 2H^+ + 2e^- \quad (4)$$

In fact it is not possible to write a reasonable anodic reaction for a mercury electrode in a sodium perchlorate–anhydrous acetic acid electrolyte which does not correspond to 100% current efficiency for hydrogen ion generation. In accordance with this, we observed no difficulty in generating hydrogen ion with 100% current efficiencies with current densities from 0.2–2.0 mA per cm².

The detection of the end-point

After soaking in acetic acid for several h, the glass electrode responded readily to changes in hydrogen ion concentration in the acetic acid–acetic anhydride solvent. A typical titration curve for the titration of *ca.* 0.03 mmoles of potassium hydrogen phthalate in a volume of 75 ml is shown in Figure 1. The potentials adopted by the glass electrode at the start of a titration were reproducible to 2–3 mV for each concentration of base used, and the end-point potentials were equally reproducible. The end-point was taken as the point of maximum slope in a plot of generation time *versus* the potential of the glass electrode.

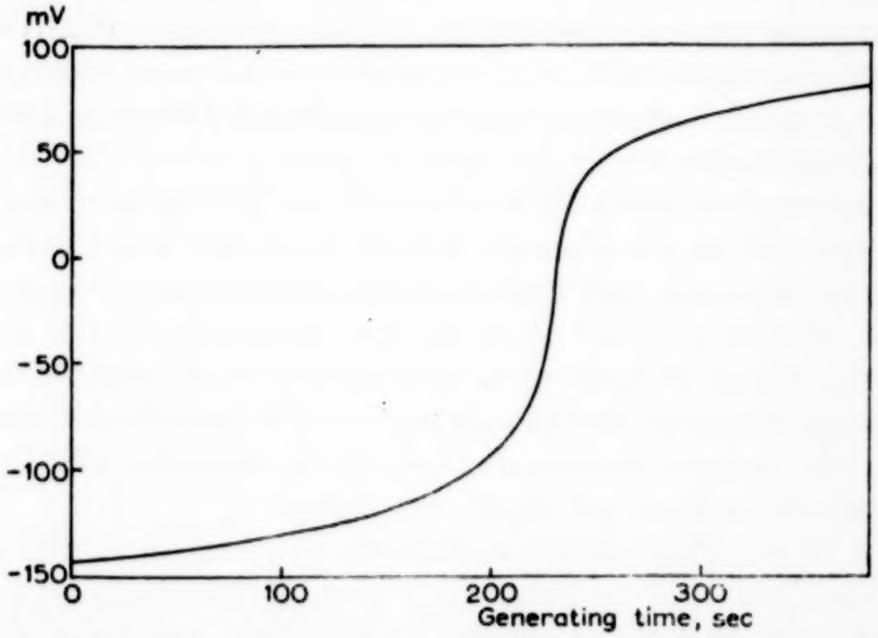

Fig. 1. Potentiometric titration curve for 0.03 mmoles of potassium hydrogen phthalate in 75 ml of acetic acid–acetic anhydride solvent. The ordinate gives the potential observed between the glass electrode and the mercury–mercurous acetate reference electrode. The generating current was 15.62 mA.

When quantitites of base greater than about 0.01 mequiv. were titrated it was observed in the vicinity of the end-point that the potential of the glass electrode did not achieve a steady value for several min after the generation of hydrogen ion had ceased. For such cases it was necessary to generate about 95% of the equivalent amount of hydrogen ion, to wait 5–10 min, and then generate in small increments, with a 2–3 minute pause after each increment, until the potential of the glass electrode was stable. Unless this waiting procedure was followed, the results were consistently 2–5% high. The reasons for the slow approach to equilibrium near the end-point are not clear and a study of this phenomenon is in progress.

Solvent system

The supporting electrolyte used for the coulometric generation consisted of a mixture of six parts (by volume) acetic anhydride and one part acetic acid, which was also 0.1 *F* in sodium perchlorate. The large amount of acetic anhydride was advantageous for four different reasons. First, as pointed out by STREULI[7], many substances display stronger basic properties in an acetic anhydride solvent than in acetic acid. Our observations confirmed this for potassium hydrogen phthalate and sodium acetate. Sharper end-points were obtained in the mixed solvent than in acetic acid alone.

A second advantage of the acetic anhydride stems from its dielectric constant which is over twice as great as that of glacial acetic acid. As a result, the sodium perchlorate is more ionized in the mixed solvent and the conductivity of the 0.1 *F* sodium perchlorate solution is about ten times greater than is a saturated (*ca.* 0.6 *F*) solution of sodium perchlorate in acetic acid. This greater conductivity makes it much simpler to maintain a constant generating current with the mixed solvent solution than when the supporting electrolyte is prepared from pure acetic acid.

It was found that the addition of sodium perchlorate to acetic acid solutions of weak bases caused such a large depression in the potential inflection at the end-point that the precision with which a titration could be carried out was seriously reduced. In the mixed acetic acid–acetic anhydride solvent, however, this undesirable effect of the sodium perchlorate was much less pronounced and precise titrations resulted.

Finally, the presence of even small amounts of water in a glacial acetic acid solvent causes the end-point in an acidimetric titration to be much more poorly defined. The presence of the large excess of acetic anhydride in the mixed solvent ensures that the solvent remains virtually completely anhydrous.

Blank titrations and corrections

The 0.1 *F* sodium perchlorate supporting electrolyte solution used for the generation of hydrogen ion was observed to contain small amounts of basic impurities (*ca.* $2 \cdot 10^{-5}$ mequivs. per ml). These impurities were corrected for by pretitrating the supporting electrolyte to a potential inflection, adding the aliquot of standard base, and continuing the titration to a second potential inflection. The time between the first and second inflections corresponded to the amount of base present. The anhydrous acetic acid which was used to prepare the standard solutions of bases was observed also to contain a very small amount of basic impurity (*ca.* 10^{-6} mequivs. per ml). The size of this impurity was determined by titrating volumetrically a large sample of the acetic acid to an indicator end-point[5]. A correction for this basic impurity in the acetic acid was applied to the titrations of aliquots of the standard solutions of base.

Results

Table I summarizes the results obtained for titrations of standard solutions of potassium hydrogen phthalate and sodium acetate. The sodium acetate was prepared by dissolving sodium carbonate in acetic acid.

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The maximum quantity of base that could be titrated was fixed by the fact that with quantities of base greater than about 0.3 mequivs. in 90 ml, the waiting time required for the glass electrode to reach a steady potential became prohibitively long and the titration was no longer practical. The lower limit of the titration is about $3\ 10^{-4}$ mequivs. of base because for smaller quantities the potential inflection at the end-point becomes too gradual for precise determinations to be made.

Extensions of the titration

In principle, the method for the coulometric generation of hydrogen ion described here should be applicable to the titration of many of the basic substances which are titratable volumetrically in acetic acid. Exceptions would include those substances, such as easily acylated amines, which react with acetic anhydride to form non-basic products.

TABLE I

Base taken mequivs·10³	*Number of titrations*	*Base found mequivs·10³*	*% error*
Potassium hydrogen phthalate–amalgam electrode			
18.73	7	18.72 ± 0.01	−0.06
37.08	4	37.08 ± 0.02	0.00
92.91	3	92.88 ± 0.03	−0.03
Sodium acetate–amalgam electrode			
0.316	4	0.312 ± 0.008	−1.3
0.627	3	0.634 ± 0.005	+1.1
2.81	4	2.81 ± 0.00	0.00
5.57	3	5.57 ± 0.01	0.00
13.94	3	13.94 ± 0.02	0.00
48.00	2	48.00 ± 0.02	0.00
Sodium acetate–mercury pool electrode			
48.00	3	47.98 ± 0.04	−0.02
94.95	4	94.91 ± 0.05	−0.04
237.9	3	237.9 ± 0.1	0.00
332.9	1	332.6	−0.09

A coulometric titration of fluoride ion has been accomplished with this technique and the details of the titration will be described in a forthcoming publication.

The coulometric generation of hydrogen ion in acetic acid–acetic anhydride mixtures would be more convenient and straightforward if the mercury anode could be replaced by a platinum generator anode. The oxidation of acetic acid at a platinum anode would provide a means for generating hydrogen ions with 100% current efficiency if the electrode reaction were reaction (3) or (4). However, it was not found possible to generate hydrogen ion with current efficiencies greater than about 95% by oxidizing the acetic acid–acetic anhydride mixture at a platinum anode. The side reactions which are responsible for the decreased current efficiencies have yet to be established. The possibility that hydrogen ion could be generated by oxidizing species such as hydroquinone, formic acid, or acetaldehyde at a platinum anode is presently under investigation. Preliminary experiments have shown that the oxidation of hydrobenzoquinone to benzoquinone and hydrogen ion does proceed with 100% titration efficiency at a platinum electrode in the acetic acid–acetic anhydride solvent system.

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SUMMARY

A technique for the coulometric generation of hydrogen ions in an acetic acid–acetic anhydride–sodium perchlorate electrolyte by anodically oxidizing a mercury electrode is described. Accurate coulometric titrations of sodium acetate and potassium hydrogen phthalate have been carried out. The technique should be applicable to many of the basic substances which can be titrated volumetrically in acetic acid.

RÉSUMÉ

Les auteurs proposent une technique de titrages acidimétriques par coulométrie dans l'acide acétique anhydre. On a pu effectuer ainsi des dosages précis d'acétate de sodium et de biphtalate de potassium. Applications possibles également pour de nombreux autres composés basiques.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur coulometrischen Erzeugung von Wasserstoffionen in einem Essigsäure-Essigsäureanhydrid-Natriumperchlorat Elektrolyt und deren Anwendung zur coulometrischen Titration von Natriumacetat und Kaliumhydrogenphtalat. Weitere Anwendungsmöglichkeiten werden erwähnt.

REFERENCES

[1] J. J. LINGANE, "*Electroanalytical Chemistry*", 2nd. Ed., Interscience Publishers, Inc., New York 1958, p. 613.

[2] A. S. MEYER, JR. AND C. M. BOYD, *Anal. Chem.*, 31 (1959) 215.

[3] C. A. STREULI, *Anal. Chem.*, 28 (1956) 130.

[4] R. B. HANSELMAN AND C. A. STREULI, *Anal. Chem.*, 28 (1956) 918.

[5] J. S. FRITZ, "*Acid-Base Titrations in Non-aqueous Solvents*", G. Frederick Smith Chemical Company, Columbus, Ohio 1952, p. 9–23.

[6] J. J. LINGANE, *Anal. Chem.*, 26 (1954) 1021.

[7] C. A. STREULI, *Anal. Chem.*, 30 (1958) 997.

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GAS–LIQUID CHROMATOGRAPHIC ANALYSIS OF AROMATIC HYDROCARBONS BOILING UP TO 218° IN A LOW-TEMPERATURE COAL TAR*

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INTRODUCTION

Detailed analysis of low-temperature coal tar will lead to clearer understanding of the chemical structure of the tar and thus help both in the study of the mechanism of carbonization and the development of uses for the tar.

As a part of a broad low-temperature coal tar characterization program, this paper presents the results of analysis of the aromatic hydrocarbons, boiling up to 218°, present in the neutral oil portion of a low-temperature bituminous coal tar.

Previously only 28 aromatic hydrocarbons boiling between 80–218° were found in low-temperature bituminous coal tars by means of older analytical techniques[1-4]. In 1956 GRANT AND VAUGHAN[5] described the gas–liquid chromatographic analysis of aromatic hydrocarbons in coal tar naphthas and identified benzofuran, an unspecified methyl styrene, and six other aromatic hydrocarbons boiling up to 178° in two low-temperature coal tars; of these, only the methyl styrene was not previously reported.

In the present work, gas–liquid chromatography and other modern techniques were used for analysis; 52 aromatic hydrocarbons boiling up to 218° were found in a low-temperature bituminous coal tar, and their quantities were determined.

A correlation was established between relative retention and boiling points for some alkyl benzenes, whereby identification of several other aromatic hydrocarbons was made possible.

Besides indans, benzofurans, and indenes the aromatic hydrocarbons identified are methylated, ethylated, or propylated benzenes. Up to the present, no butyl benzenes have been found in this particular tar. Of the 52 compounds found, 27 had not been previously reported to be present in a low-temperature bituminous coal tar.

Another phase of the work concerning analysis of higher boiling aromatic hydrocarbons, such as biphenyls and alkyl naphthalenes, several of which have already been identified in this laboratory, is being completed and the results will be reported later.

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EXPERIMENTAL WORK AND RESULTS

I. Preparation of aromatic hydrocarbon concentrates from the coal tar for gas–liquid chromatography

Isolation of neutral oil from tar distillate. The tar used in this work was made from a West Virginia, Pittsburgh-seam, high-volatile bituminous coal in a fluidized carbonization pilot plant at about 480–510°. The raw tar was deashed, dehydrated, and topped to about 175° at the plant. The tar distillate had been obtained in this laboratory under very mild temperature conditions calculated to be equivalent to about 350–360° at atmospheric pressure with a yield of 20.8 weight-percent of the tar in the main distillate and less than 1% collected in a dry ice trap.

About 3 l (2660 g) of the main distillate were extracted according to the method of FISHER AND EISNER[6] to remove tar acids and tar bases. The neutral oil thus obtained was washed three times with an equal volume of water. After it had been passed through a filter made of three layers of filter paper on a funnel, the oil was dried in a desiccator over anhydrous calcium chloride for a week. About 2400 ml (2180 g) of dry neutral oil, corresponding to 82% by weight of the distillate and 16.9% by weight of the tar, was obtained.

Fractional distillation of the neutral oil. A 698-g charge of the neutral oil was fractionally distilled in a PODBIELNIAK Hyper-Cal high-temperature automatic distillation apparatus. The column was 8 mm by 36 inches and was packed with Heli-Grid packing. The end-point chosen for this distillation was a pot temperature of 200° to avoid any significant thermal alterations. The results of this distillation are given in Table I. Equivalent atmospheric boiling points were estimated from a standard nomograph.

Separation of the neutral oil fractions into chemical types by displacement chromatography. The silica gel adsorption method based on displacement chromatographic techniques, which have been applied to petroleum distillates[7] and shale-oil naphthas[8], was adapted for separating the aromatic hydrocarbons from saturates and unsaturates.

The column chosen for this work consisted of an upper section 22 cm long and 10 mm I.D. and a lower section 138 cm long and 3 mm I.D. The entire column was jacketed to provide water for cooling or heating as required.

The column was packed with Davison Grade 950 silica gel, 60–200 mesh, which had been freshly activated at 160° for 4 h just before packing. About 26 g of silica gel were needed for the column. A fresh batch of silica gel was used for each run.

The sample was charged to the column, using about 3 p.s.i.g. oxygen-free nitrogen pressure. The desorbents selected were two different alcohols, the choice being made on the basis of the relative kinematic viscosities of the sample and the alcohol. An alcohol could be selected for each fraction so that its viscosity would be somewhat greater than that of the fraction. The alcohols were also chosen for desorbents on the basis of miscibility with the samples, and ease of removal from the last portions of the charge desorbed. After the sample was charged to the column, it was followed immediately by the desorbent with about 10 p.s.i.g. nitrogen pressure.

The operating temperature chosen for each sample depended on the melting points

TABLE I

FRACTIONATION OF NEUTRAL OILS IN PODBIELNIAK STILL

Charge: 16.92 wt.-% of the tar
698 g
Distillate: 360 g = 51.6%
Residue: 338 g = 48.4%

Fraction No.	*Head temperature °C, 50 mm*	*Estimated b.p. °C, 760 mm*	*Weight g*
1	77.5– 87.5	163–180	4.43
2	87.5– 94.0		
3	94.0–101.4	180–190	3.94
4	101.4–104.3	190–192	4.53
5	104.3–109.0	192–198	9.81
6	109.0–114.5	198–202	9.61
7	114.5–118.3	202–210	25.95
8	118.3–121.8		
9	121.8–124.2	210–213	5.29
10	124.2–126.5	213–220	17.88
11	126.5–130.9		
12	130.9–132.9	220–225	14.80
13	132.9–134.2		
14	134.2–137.3	225–230	12.78
15	137.3–139.9	230–233	18.36
16	139.9–141.5	233–235	17.11
17	141.5–141.9	235–236	14.13
18	141.9–145.9	236–240	11.54
19	145.9–149.4	240–243	18.46
20	149.4–151.6	243–246	18.84
21	151.6–153.5	246–248	19.22
22	153.5–155.0	248–250	20.57
23	155.0	250	18.55
24	155.0–155.8	250–251	6.34
25	155.8–157.8	251–253	18.46
26	157.8–158.0	253–253	18.46
27	158.0–159.9	253–254	18.07
28	159.9–162.0	254–256	21.34
29	162.0–163.0	256–260	11.53
		Total	360.00

of the expected components in the fraction. If some of them were crystalline at room temperature, a temperature near the melting points of the components was used.

Fractions were obtained with an automatic fraction collector which counted drops photoelectrically and maintained the fractions in an atmosphere of oxygen-free nitrogen.

Usually only the very last fraction was contaminated by the desorbent. The desorbent was removed by extracting with 80 to 90% glycerin, and the glycerin was then removed with several water washings. The alcohol- and glycerin-free sample was dried overnight over anhydrous calcium chloride in a partly evacuated desiccator. The refractive index was obtained on each fraction, and by comparing these values with literature values for pure hydrocarbons in the boiling range of the charge it was readily estimated where the paraffins and naphthenes, olefins, aromatics, and neutral oxygen, nitrogen and sulfur compounds were located among the fractions. With this technique, no sharp borderlines could be expected between two adjacent types. However, it was found that overlapping occurred only in the very first and the very last fractions of any one type.

Since this paper covers the first six distillate fractions boiling from 163°–202°, the data on displacement chromatography for only these fractions are given in Table II. About 17 drops per displacement fraction were collected, except for the last one, which consisted of about 50 drops.

II. Analysis of aromatic hydrocarbons by gas–liquid chromatography

Apparatus and operating conditions. A Perkin-Elmer model 154C Vapor Fractometer was used. The response range of the recorder was 0–11 mV, and the speed of the chart was 3.75 in./h. The peak areas produced by components of the sample on the chromatogram were measured with a planimeter.

The column for this work was made from a 15-ft. × $^1/_4$-in. O.D. copper tubing filled with approximately 50 g of packing made of 25% Apiezon L grease on 30–60 mesh fire brick. After being packed, the column was coiled to fit into the column chamber of the Fractometer.

The temperature chosen for the analysis was 150°, approximately 10° below the lowest boiling fraction and 50° below the highest boiling fraction. Samples were injected with 10 or 50 μl-syringes. The carrier gas was helium, admitted to the column at a pressure of 12 lb./in.^{2}, corresponding to a flow rate of 95 ml/min. The outlet pressure was atmospheric. The voltage for the bridge of the thermoconductivity detector was 8 V, and the most sensitive range was used. Throughout the work the temperature stayed within ± 0.1°, and the carrier gas pressure and the voltage of the bridge stayed constant.

The efficiency of the column under these conditions, referring to *n*-propylbenzene and to 1,2,3,5-tetramethylbenzene, was 3520 and 3885 theoretical plates, respectively, calculated by using the equation[9], No. of theoretical plates $= 16(x/y)^2$, where $y =$ length of peak baseline (as defined), and $x =$ length from start of run to middle of baseline section.

Sample collecting system for gas–liquid chromatography. The original fraction collecting system for the Perkin-Elmer instrument has a short length of 1/8-in. stainless-steel tubing leading from the detector cell to an external syringe needle adapter that has a three-way syringe valve. This is intended for attaching a short needle, which can be inserted through a rubber serum bottle cap at the bottom of a solvent-filled tube for washing effluent gas in order to collect fractions. However, this type of collector was found to be unsatisfactory in most instances.

A new fraction-collecting system was devised, which would take advantage of the existing needle adapter. This involved heating the stainless-steel tubing electrically to prevent the fractions from condensing, and using 6-in , 18-gauge syringe needles cooled with powdered dry ice as fraction collectors. Holders for dry ice powder were made from 110-mm lengths of 18-mm O.D. glass tubing, which were wrapped with aluminum foil and asbestos string, and plugged at one end with 12 mm thick cork stoppers, each having a small hole in the center for entry of the needles. To collect the material producing a chromatogram peak, one of the needles was fastened to the upright needle adapter and one of the dry ice jackets was slipped down over the needle, the insulating cork plug resting on the hot needle hub. The jacket was carefully packed with dry ice powder and the three-way valve turned to admit effluent gas to the needle. After a sample was collected, the needle was removed, a Teflon plug

TABLE II

DISPLACEMENT CHROMATOGRAPHIC SEPARATION OF NEUTRAL OIL DISTILLATE FRACTIONS INTO CHEMICAL TYPES

Distillate fraction No.	1 + 2	3	4	5	6
Weight of charge, g	1.77	3.15	3.60	7.40	7.70
Desorbent	Isopropyl alcohol	Isopropyl alcohol	Isopropyl alcohol	Isopropyl alcohol	Butyl alcohol
Saturates + some olefins:					
Number of fractions	5	3	4	7	5
Refractive index range, n_d^{20}	1.3930 – 1.3941	1.4381 – 1.4832	1.4252 – 1.4471	1.4328 – 1.4695	1.4400 – 1.4683
Total weight, g	0.74	0.61	1.20	2.11	1.93
Aromatics + some olefins + some O,S compounds:					
Number of fractions	4	5	5	9	12
Refractive index range, n_d^{20}	1.3941 – 1.5007	1.4832 – 1.5310	1.4911 – 1.5397	1.4912 – 1.5545	1.4895 – 1.5601
Total weight, g	0.70	2.29	2.17	4.32	5.21
N, S, and O compounds retained on column, g	0.33	0.25	0.23	0.97	0.56
Weight of aromatic hydrocarbons identified by GLC, g	0.57	1.95	1.66	4.30	4.81

inserted at the hub end, and a little polyethylene tube slipped over the needle end and placed in a Dewar flask containing dry ice. The infrared spectrum of the sample was subsequently obtained in a 0.05 or 0.1-mm microcell for identification of the components. The infrared microcell was filled by inserting the needle tip into the cell and introducing a fraction of a drop of carbon disulfide into the needle hub. However, in some instances it was necessary to wash out the needle with about $^1/_2$ ml carbon disulfide, collecting the solution in a 1-ml beaker and carefully evaporating off solvent with a gentle stream of nitrogen until about 1 drop of solution remained. This was then placed in the microcell by capillary action, using the capillary tubing of the cell. Good infrared spectra were obtained with about 1 mg hydrocarbon, in particular, there was no contamination from compounds producing adjacent peaks.

General approach for identification. The retention times of 42 aromatic hydrocarbons boiling in the range of the neutral oil samples were obtained for preliminary identification of the unknowns. The relative retentions at 150° and 200° of the 42 aromatics, referred to *n*-propylbenzene, are shown in Table III. These relative retention values can be considered to be either relative retention times or relative retention volumes.

The aromatic fractions obtained by displacement chromatography of the first six distillate fractions were examined individually by gas–liquid chromatography under the same conditions for the known compounds. To confirm the identification the material producing each peak was collected for infrared spectrophotometric analysis. Three methods were used to identify the aromatic hydrocarbons present in the fractions.

The first method of identification consisted of a combination of conventional gas–liquid chromatography and infrared spectrophotometry. The retention times of unknown peaks were compared with those of known compounds for preliminary identification. The material producing each peak was then collected in a microcell for an infrared spectrum, as previously described. The confirmation of identity was then made by comparing this spectrum with that of the known compound.

Retention times could not, of course, be obtained for those compounds for which authentic specimens were not available. A second method of identification was used for these compounds which involved the correlation curves of relative retentions and boiling points; these are shown in Fig. 2 and explained in detail in a later section. Boiling points of the unknowns producing peaks were obtained from their relative retentions by these correlation curves and were used as a preliminary means of identification. Since literature infrared spectra of a number of compounds were available, conformation could be made in these instances.

For a third group of compounds, neither the retention times nor the infrared spectra of authentic specimens were available. However, from the correlation curves and the relative retentions of the unknown peaks, tentative identification could be made through the boiling points. Also, by correlating infrared absorption bands and molecular structures, these tentative identities could be substantiated further.

To illustrate the first and second methods of identification, the chromatogram of a typical fraction is shown in Fig. 1, and the boiling points of the components producing the peaks (as obtained from the correlation curves) are presented in Table IV. Excellent agreement is shown between literature and predicted boiling points. The

TABLE III

LITERATURE BOILING POINTS, RELATIVE RETENTIONS AND CALIBRATION FACTORS (f_C) OF SOME AROMATIC HYDROCARBONS

Compound	*Literature b.p. °C 760 mm*[a]	*Relative*[b] *retention (150°)*	f_C *(150°)*[c]	*Relative*[b] *retention (200°)*
Methylbenzene	110.626	0.36	1.02	0.48
Ethylbenzene	136.186	0.62	0.95	0.64
1,4-Dimethylbenzene	138.351	0.67	0.98	0.70
1,3-Dimethylbenzene	139.104	0.68	1.00	0.71
1,2-Dimethylbenzene	144.411	0.77	1.01	0.82
Isopropylbenzene	152.392	0.83	1.02	0.86
n-Propylbenzene	159.217	1.00	1.00	1.00
1-Methyl-3-ethylbenzene	161.305	1.06	1.01	—
1-Methyl-4-ethylbenzene	161.989	1.09	1.08	1.06
1-Methyl-2-ethylbenzene	165.153	1.21	1.06	1.17
1,3,5-Trimethylbenzene	164.716	1.19	1.08	1.13
1,2,4-Trimethylbenzene	169.351	1.38	1.03	1.29
1,2,3-Trimethylbenzene	176.084	1.67	1.04	1.52
Indan	177.82	1.82	1.65	1.69
Isobutylbenzene	172.759	1.33	1.07	1.26
sec.-Butylbenzene	173.305	1.34	1.08	1.27
n-Butylbenzene	183.27	1.77	1.04	1.56
1-Methyl-3-isopropylbenzene	175.14	1.39	1.07	1.27
1-Methyl-4-isopropylbenzene	177.10	1.48	1.04	1.35
1-Methyl-2-isopropylbenzene	178.15	1.58	0.94	1.42
1-Methyl-3-*n*-propylbenzene	181.80	1.71	1.03	1.51
1-Methyl-4-*n*-propylbenzene	183.30	1.76	1.03	1.58
1-Methyl-2-*n*-propylbenzene	184.80	1.90	1.07	1.67
1,3-Diethylbenzene	181.102	1.62	1.00	1.45
1,2-Diethylbenzene	183.423	1.81	1.06	1.60
1,4-Diethylbenzene	183.752	1.79	1.03	1.58
1,3-Dimethyl-5-ethylbenzene	183.75	1.82	1.09	1.59
1,2,4,5-Tetramethylbenzene	196.80	2.77	0.93	2.28
1,2,3,5-Tetramethylbenzene	198.00	2.87	1.06	2.33
Indene	182.44	1.92	1.10	1.80
1-Methylindene	199	2.22	1.20	1.98
2-Methylindene	208	3.48	1.15	2.96
1-Methyl-3,5-diethylbenzene	200.70	2.68	1.11	2.14
1,2,3,4-Tetrahydronaphthalene	207.57	3.84	2.05	3.13
1,4-Diisopropylbenzene	208.9	3.26	—	2.49
1,2-Diisopropylbenzene	209	3.06	—	2.51
Benzofuran	171.38	1.35	1.15	1.33
Naphthalene	217.96	4.68	1.14	3.51
1,3,5-Triethylbenzene	216.2	3.87	—	1.13
Pentamethylbenzene	231.8	7.08	—	4.87
α-Methylstyrene	165.5	1.22	1.11	1.14
β-Methylstyrene (*trans*)	178.26	1.64	1.09	1.47

TABLE III (continued)

Compound	*Literature b.p. °C 760 mm*[a]	*Relative*[b] *retention (150°)*	f_c *(150°)*[c]	*Relative*[b] *retention (200°)*
1,4-Dimethyl-2-ethylbenzene	186.91	2.04[d]	—	1.73[d]
1,2-Dimethyl-4-ethylbenzene	189.75	2.17[d]	—	1.89[d]
1-Methylindan	190.6	2.30[d]	—	1.99[d]
1,2-Dimethyl-3-ethylbenzene	193.91	2.50[d]	—	2.06[d]
5-Methylindan	202.0	3.25[d]	—	2.67[d]
1-Methyl-3,4-diethylbenzene	203.6	3.00[d]	—	—
4-Methylindan	205.5	3.46[d]	—	2.81[d]
1,2,3,4-Tetramethylbenzene	205.04	3.48[d]	—	2.81[d]
3-Methylindene	205	3.50[d]	—	2.82[d]

[a] All values, except for benzofuran, from API Research Project 44, *Selected Values of Properties of Hydrocarbons and Related Compounds*, Carnegie Institute of Technology, Pittsburgh, Pa. Benzofuran b.p. from J. N. BRESTON and A. W. GAUGER, *Proc. Am. Gas Assoc.*, 28 (1946) 492.

[b] Dead volume corrected.

[c] Defined in eq. 1.

[d] The relative retentions of these compounds were determined from tar components identified by I.R.

peak numbers in Fig. 1 are explained in Table IV. This chromatogram was produced by a 10-μl sample of an aromatic cut of $n_d^{20} = 1.5074$, from distillate fraction 5 in a boiling range of 192–198°. Peak 1 is produced by *n*-propylbenzene, the internal standard, added to the cut for quantitative estimation of the components. The components producing peaks 2, 3, 4, 9, 10 and 11 were identified by comparing the retention times with those of known compounds. The components producing peaks 5, 6, 7, 8, 12, 13 and 14 were identified through their boiling points, obtained from their

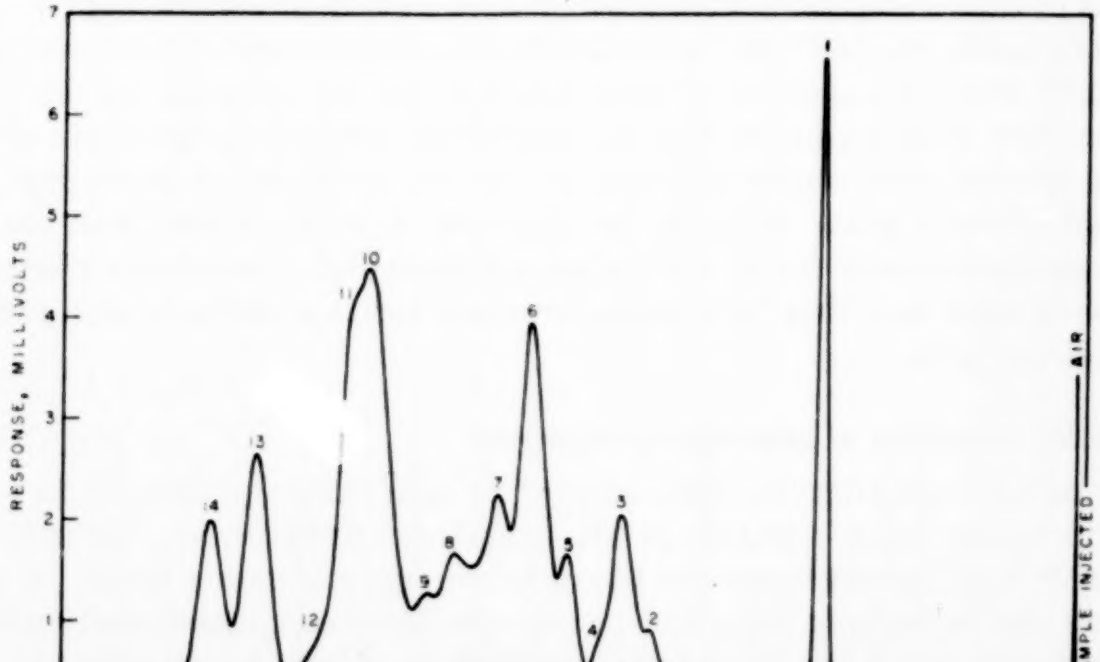

Fig. 1. Chromatogram of an aromatic cut obtained from distillate fraction 5.

TABLE IV

IDENTIFICATION OF COMPONENTS PRODUCING ELUTION PEAKS IN THE GLC OF AN AROMATIC CUT FROM DISTILLATE FRACTION 5

Peak No.	*Relative retention*	*Compound identified*	*Relative retention of known compound*	*Boiling point °C*	
				from literature	*from correlation curve*
1	1	*n*-Propylbenzene (added standard)	1	159.2	159.2
2	1.69	1-Methyl-3-*n*-propylbenzene	1.71	181.8	181.3
3	1.82	1,3-Dimethyl-5-ethylbenzene	1.82	183.8	183.7
4	1.89	1-Methyl-2-*n*-propylbenzene	1.90	184.8	184.9
5	2.02	1,4-Dimethyl-2-ethylbenzene	*	186.9	186.1
6	2.16	1,2-Dimethyl-4-ethylbenzene	*	189.8	189.3
7	2.29	1-Methylindan	*	190.6	191.3
8	2.46	1,2-Dimethyl-3-ethylbenzene	*	193.9	193.5
9	2.65	1-Methyl-3,5-diethylbenzene	2.68	200.7	200.1
10	2.79	1,2,4,5-Tetramethylbenzene	2.77	196.8	197.6
11	2.86	1,2,3,5-Tetramethylbenzene	2.87	198.0	198.4
12	3.00	1-Methyl-3,4-diethylbenzene	*	203.6	204.1
13	3.25	5-Methylindan	*	202.0	202.6
14	3.45	4-Methylindan	*	205.5	204.5

* Authentic specimens not available for determination of retention times.

relative retention and the correlation curves. To confirm the identities, a 25 μl-sample was used to produce enough material for each major peak for infrared spectrophotometric analysis. However, the minor ones, such as 4, 8, 9 and 12, were better confirmed by the infrared spectra of the material producing the corresponding peaks in the chromatogram of an adjacent aromatic cut.

Table V illustrates the third method of identification. It is to be noted that the identities of three compounds were substantiated further by considering the infrared absorption bands and probable molecular structures according to the correlations of BELLAMY[10]. Two compounds were present in the last two distillate fractions (Nos. 5 and 6) in such small quantities that no satisfactory infrared spectra were obtained. Infrared spectra were obtained, however, for the components producing all the significant chromatogram peaks. It was observed that only a few weak absorption bands were unaccounted for by the compounds identified. The relative intensities of these bands were such that these unknown components could have been present in only trace amounts.

Quantitative estimation of aromatic hydrocarbons

The internal standard method was adapted for quantitative analysis of the samples, *n*-propylbenzene being selected as the standard. KEULEMANS, KWANTES AND RIJNDERS[11] have demonstrated the use of an average calibration factor, f_C, defined as follows, for calibrating areas and percentages for a component, and an internal standard for obtaining precise quantitative analysis of light hydrocarbons:

$$f_C = A_s W_c / A_c W_s \quad \ldots\ldots\ldots\ldots \quad (1)$$

where A_s and A_c are the areas for the internal standard and component in the

TABLE V

DATA FOR TENTATIVE IDENTIFICATION OF FIVE ALKYLBENZENES

Name of compound	*Literature b.p. °C 760 mm*	*Relative retention of the unknown peak*	*B.p. °C obtained from the correlation curve*	*Infrared spectral-structural correlations*
1,4-Dimethyl-2-isopropylbenzene	196.2	2.38	196.6	—
1,3-Dimethyl-2-*n*-propylbenzene	207.6	3.35	207.7	—
1,4-Dimethyl-2-*n*-propylbenzene	203.6	3.04	204.6	12.23 μ(S): 2H out-of-plane deformation vibration. 11.39 μ(M): 1H out-of-plane deformation vibration. 9.12 μ(W): 9.47 μ(W); 9.90 μ(MW) suggest 1,2,4-substitution of benzene ring. Probable structure: 1,2,4-trialkylbenzene.
1-Methyl-2,4-diethylbenzene	205.0	3.10	205.2	12.40 μ(S): 2H out-of-plane deformation vibration. 11.30 μ(M): 1H out-of-plane deformation vibration. 9.60 μ(W); 9.70 μ(W); and 8.65 μ(W) suggest 1,2,4-substitution of benzene ring. Probable structure: 1,2,4-trialkylbenzene.
1,2-Dimethyl-3-*n*-propylbenzene	210.7	3.64	210.5	12.81 μ(S) and 14.32 μ(M): 3H out-of-plane deformation vibration. 8.67 μ(W): 1,2,3-substitution of benzene ring. Probable structure: 1,2,3-trialkylbenzene.

mixture, and W_c and W_s are the weight-percentages of the component and the standard.

In order to investigate the deviation of the average calibration factors of aromatic hydrocarbons from the actual values in a certain range of concentrations, eight pure compounds (namely, 1-methyl-3-ethylbenzene, 1,3,5-trimethylbenzene, indan, 1,3-diethylbenzene, indene, 1,3-dimethyl-5-ethylbenzene, 1,2,3,5-tetramethylbenzene, and 1,2,3,4-tetrahydronaphthalene) were used. Three solutions of each compound in different concentrations, about 15, 30, and 60% by weight, were prepared in *n*-propylbenzene. Using these 24 solutions, the f_c values were then calculated from the weight-percentages and the peak areas produced by the components in their chromatograms. It was found that the average f_c in the concentration range of 15–60% by weight had a maximum deviation of only about ± 3% from the actual values, and the best results were obtained at concentration ranges of 30–60%. This is considered accurate enough for estimating the amounts of aromatic components present in such a complex mixture as coal tar. The f_c values for the rest of the aromatic hydrocarbons were determined only once at 150° at a concentration of 40–50%. These f_c values are shown in Table III and were used to determine the weight percentages of all aromatic hydrocarbons in the fractions. For those compounds which were not available in this laboratory but found to be present in the sample, the f_c value of its isomers or of a structurally similar compound was used.

Two synthetic blends were analyzed by using these f_c values, and the results are shown in Table VI.

For analyzing the components in the sample, a certain amount of the internal standard, *n*-propylbenzene, roughly 15% by weight, was added to each of the sample fractions so that the peak area of the standard approximately equaled that of the major peaks. A new chromatogram of each fraction, after the addition of the standard, was then made. The percentage of each component was then calculated by using

TABLE VI

ANALYSIS OF SYNTHETIC BLENDS

Blend	*Component*	*Relative retention*	*Wt. % present*	*Wt. % found*		
				Run 1	*Run 2*	*Run 3*
A	Isopropylbenzene	0.82	10.28	10.31	10.47	10.77
	n-Propylbenzene	1.00	11.67	—	—	—
	1,3,5-Trimethylbenzene	1.29	12.93	12.91	12.82	12.61
	1-Methyl-2-isopropylbenzene	1.56	12.62	12.14	12.16	12.54
	Indan	1.82	19.07	18.08	18.60	18.34
	Indene	1.92	14.71	15.03	15.05	14.67
	1,2,3,5-Tetramethylbenzene	2.88	18.72	19.16	19.19	18.66
	Total		100.00	99.30	99.96	99.26
B	*n*-Propylbenzene	1.00	14.64	—	—	—
	sec.-Butylbenzene	1.35	18.14	17.62	17.42	—
	1-Methyl-4-isopropylbenzene	1.48	15.23	14.91	14.97	—
	1-Methyl-3-*n*-propylbenzene	1.72	17.07	16.97	17.09	—
	1,3-Dimethyl-5-ethylbenzene	1.84	21.37	21.28	21.54	—
	1-Methylindene	2.23	13.64	13.54	13.76	—
	Total		100.00	98.96	99.42	—

equation (1). In the few instances of unresolved components, conventional quantitative infrared analysis was used.

The aromatic hydrocarbons found in the low-temperature bituminous coal tar and their quantities are presented in Table VII. The values of wt.% in neutral oil for the highest boiling components are not entered, since it is expected that more of these compounds will be found in distillate fractions 7 and 8.

DISCUSSION

Correlation between relative retention and boiling points of alkylbenzenes having an equal number of carbon atoms

DESTY AND WHYMAN[12] plotted the boiling points of a large number of low-boiling paraffinic hydrocarbons and a few aromatic hydrocarbons against the logarithm of their relative retention volumes for two different stationary phases, resulting in two almost straight lines for each of the solvents. These plots indicate the selectivity of the two stationary phases for these two different types of solutes and offer help in choosing a suitable solvent for the separation of these two general types. However, no relationship between the relative retentions and boiling points of alkylbenzenes

TABLE VII

ANALYSIS OF INDIVIDUAL AROMATIC HYDROCARBONS BOILING UP TO 200° IN NEUTRAL OIL DISTILLATE FRACTIONS

Compounds identified	*Fractions*	*Method of identification*	*Source of I.R. spectrum*	*Total wt. g*	*Wt. % in neutral oil*[a]
Methylbenzene[b]	1, 2	Rel. retention	—	1[c]	Trace
Ethylbenzene[b]	1, 2	Rel. retention	—	2[c]	Trace
1,3- and 1,4-Dimethylbenzene[b]	1, 2	Rel. retention	—	9[c]	Trace
1,2-Dimethylbenzene[b]	1, 2	Rel. retention	—	20[c]	Trace
Isopropylbenzene[b]	1, 2	Rel. retention	—	79[c]	Trace
n-Propylbenzene[b]	1, 2	Rel. retention, I.R.	[d]	250[c]	0.002
1-Methyl-3-ethylbenzene[b]	1, 2	Rel. retention, I.R.	[e]	0.010	0.001
1-Methyl-4-ethylbenzene[b]	1, 2	Rel. retention, I.R.	[e]	0.0098	0.001
1-Methyl-2-ethylbenzene[b]	1, 2	Rel. retention, I.R.	[e]	0.0075	0.001
1,2,3-Trimethylbenzene[b]	1, 2	Rel. retention, I.R.	[e]	0.3105	0.045
1,2,4-Trimethylbenzene[b]	1, 2, 3	Rel. retention, I.R.	[e]	0.2695	0.039
1,3,5-Trimethylbenzene[b]	1, 2, 3	Rel. retention, I.R.	[e]	0.1184	0.017
1-Methyl-4-isopropylbenzene	1, 2, 3, 4	Rel. retention, I.R.	[d]	0.0596	0.009
1-Methyl-3-isopropylbenzene	1, 2, 3, 4	Rel. retention, I.R.	[d]	0.0511	0.007
1-Methyl-2-isopropylbenzene	3	Rel. retention, I.R.	[d]	0.0164	0.002
1,2-Diethylbenzene	3, 4	Rel. retention, I.R.	[e]	0.0857	0.012
1,3-Diethylbenzene	3, 4	Rel. retention, I.R.	[e]	0.1009	0.015
1,4-Diethylbenzene[b]	4	Rel. retention	—	0.0062	0.001
1,2-Dimethyl-4-ethylbenzene[b]	3, 4, 5, 6	Rel. retention-b.p. correlation, I.R.	[e]	1.8139	0.260
1,4-Dimethyl-2-ethylbenzene	3, 4, 5, 6	Rel. retention-b.p. correlation, I.R.	[e]	0.7698	0.110
1,3-Dimethyl-5-ethylbenzene[b]	3, 4, 5, 6	Rel. retention, I.R.	[d]	1.6872	0.156
1,2-Dimethyl-3-ethylbenzene[b]	4, 5, 6	Rel. retention-b.p. correlation, I.R.	[e]	0.5938	0.085

TABLE VII (continued)

Compounds identified	*Fractions*	*Method of identification*	*Source of I.R. spectrum*	*Total wt. g*	*Wt. % in neutral oil*[a]
1-Methyl-3-*n*-propylbenzene	3, 4, 5	Rel. retention, I.R.	[d]	0.3180	0.046
1-Methyl-2-*n*-propylbenzene	5	Rel. retention, I.R.	[d]	0.0753	0.011
1,2,4,5-Tetramethylbenzene[b]	4, 5, 6	Rel. retention, I.R.	[d]	1.1066	0.159
1,2,3,5-Tetramethylbenzene	5, 6	Rel. retention, I.R.	[d]	1.7690	0.253
1,2,3,4-Tetramethylbenzene[b]	6	Rel. retention-b.p. correlation, I.R.	[e]	0.8852	—
Indene[b]	1, 2, 3, 4	Rel. retention, I.R.	[e]	0.2331	0.033
3-Methylindene	5, 6	I.R.	[e]	0.5378	—
Indan[b]	1, 2, 3	Rel. retention, I.R.	[d]	0.3945	0.057
1-Methylindan	3, 4, 5, 6	Rel. retention-b.p. correlation, I.R.	[f]	1.1265	0.161
5-Methylindan	5, 6	Rel. retention-b.p. correlation, I.R.	[f]	1.4976	—
4-Methylindan[b]	5, 6	Rel. retention-b.p. correlation, I.R.	[f]	1.4988	—
1,3-Dimethyl-2-*n*-propylbenzene	5	Rel. retention-b.p. correlation	—	0.0173	0.003
1,2-Dimethyl-3-*n*-propylbenzene	5, 6	Rel. retention-b.p. correlation, I.R.-structural correlation	—	0.1008	—
1,4-Dimethyl-2-*n*-propylbenzene	5, 6	Rel. retention-b.p. correlation, I.R.-structural correlation	—	0.4124	—
1,4-Dimethyl-2-isopropylbenzene[b]	5	Rel. retention-b.p. correlation	—	0.1151	0.017
1-Methyl-3,5-diethylbenzene	5, 6	Rel. retention, I.R.	[d]	0.2393	0.034
1-Methyl-2,4-diethylbenzene	6	Rel. retention-b.p. correlation, I.R.-structural correlation	—	0.6505	—
Styrene	1, 2	I.R.	[g]	0.0332	0.005
4-Methylstyrene	1, 2	I.R.	[h]	0.0225	0.003
β-Methylstyrene (*trans*)	1, 2	Rel. retention, I.R.	[d]	0.1396	0.020
3-Phenyl-1-butene	1, 2	I.R.	[g]	0.1163	0.017
1,2,3,4-Tetrahydronaphthalene	5,6	Rel. retention, I.R.	[d]	0.3171	—
Naphthalene[b]	6	I.R.	[d]	0.0886	—
Benzofuran[b]	1, 2	Rel. retention, I.R.	[d]	0.0991	0.014
5-Methylbenzofuran	3	I.R.	[g]	0.1432	0.021
6-Methylbenzofuran	3, 4	I.R.	[g]		
2-Methylbenzofuran	4	I.R.	[g]	0.1681	0.024
3-Methylbenzofuran	4	I.R.	[g]		
7-Methylbenzofuran	3, 4	I.R.	[g]	0.0785	0.011

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[a] Total neutral oil distilling up to about 360°, representing 16.92 wt.% of the total tar.

[b] Previously identified by others[1–5].

[c] Ratio to methylbenzene.

[d] This laboratory.

[e] American Petroleum Institute, Research Project 44, infrared spectral data, Carnegie Institute of Technology, Pittsburgh, Pa.

[f] JACOB ENTEL, CLARENCE H. ROUF, AND H. C. HOWARD, *Anal. Chem.*, 25 (1953) 1303.

[g] SAMUEL P. SADTLER & SON, Inc., Philadelphia, Pa.

[h] Courtesy of W. F. HAMNER, Monsanto Chemical Co., Texas City, Texas.

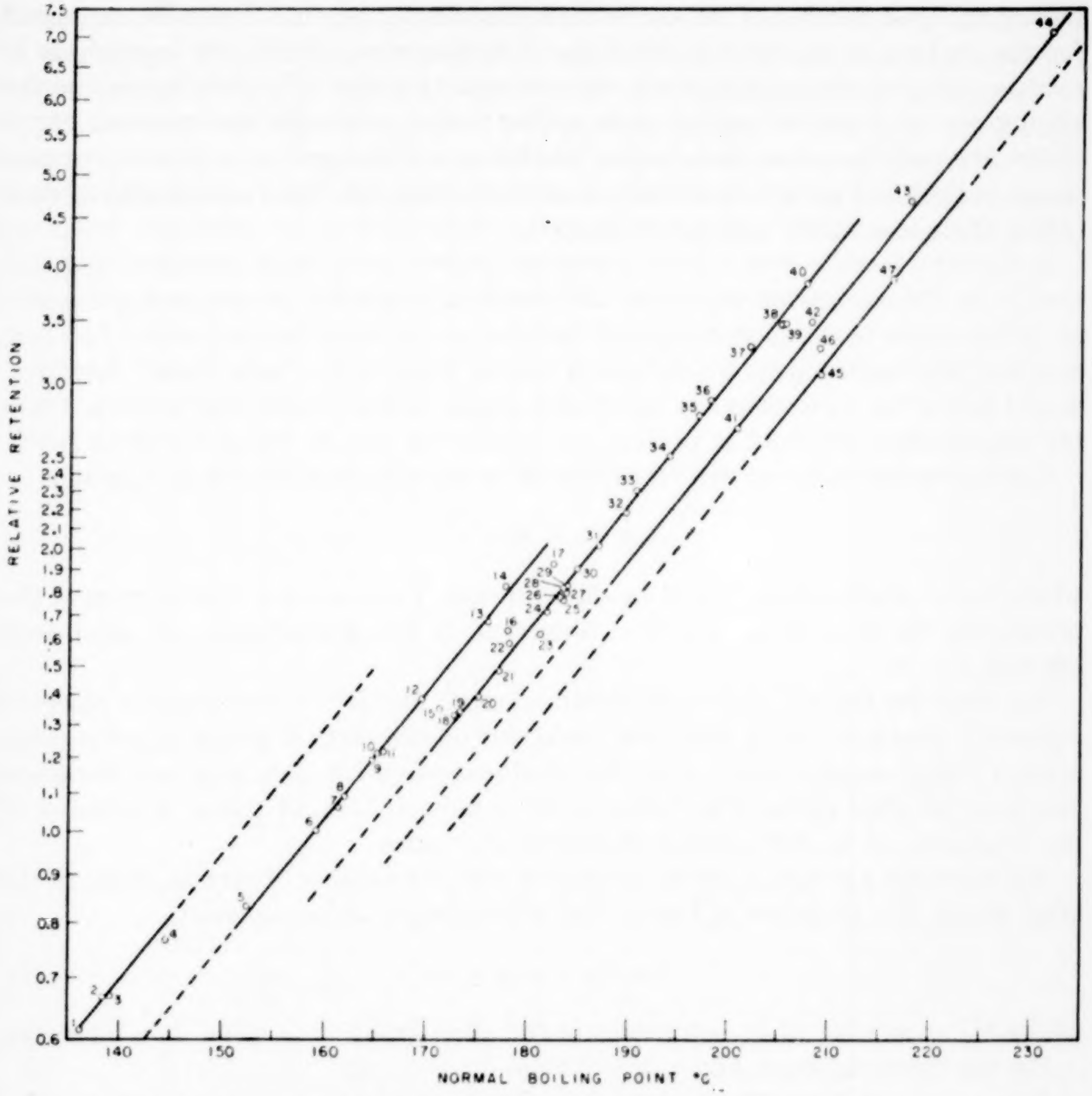

Fig. 2. Correlation between relative retentions and boiling points of some aromatic hydrocarbons at 150° on Apiezon L grease.

1. Ethylbenzene, 2. 1,4-Dimethylbenzene, 3. 1,3-Dimethylbenzene, 4. 1,2-Dimethylbenzene, 5. Isopropylbenzene, 6. *n*-Propylbenzene, 7. 1-Methyl-3-ethylbenzene, 8. 1-Methyl-4-ethylbenzene, 9. 1,3,5-Trimethylbenzene, 10. 1-Methyl-2-ethylbenzene, 11. α-Methylstyrene, 12. 1,2,4-Trimethylbenzene, 13. 1,2,3-Trimethylbenzene, 14. Indan, 15. Benzofuran, 16. β-Methylstyrene, 17. Indene, 18. Isobutylbenzene, 19. *sec.*-Butylbenzene, 20. 1-Methyl-3-isopropylbenzene, 21. 1-Methyl-4-isopropylbenzene, 22. 1-Methyl-2-isopropylbenzene, 23. 1,3-Diethylbenzene, 24. 1-Methyl-3-*n*-propylbenzene, 25. 1-Methyl-4-*n*-propylbenzene, 26. *n*-Butylbenzene, 27. 1,4-Diethylbenzene, 28. 1,2-Diethylbenzene, 29. 1,3-Dimethyl-5-ethylbenzene, 30. 1-Methyl-2-*n*-propylbenzene, 31. 1,4-Dimethyl-2-ethylbenzene, 32. 1,2-Dimethyl-4-ethylbenzene, 33. 1-Methylindan, 34. 1,2-Dimethyl-3-ethylbenzene, 35. 1,2,4,5-Tetramethylbenzene, 36. 1,2,3,5-Tetramethylbenzene, 37. 5-Methylindan, 38. 4-Methylindan, 39. 1,2,3,4-Tetramethylbenzene, 40. 1,2,3,4-Tetrahydronaphthalene, 41. 1,3-Diethyl-5-methylbenzene, 42. 2-Methylindene, 43. Naphthalene, 44. Pentamethylbenzene, 45. 1,2-Diisopropylbenzene, 46. 1,4-Diisopropylbenzene, 47. 1,3,5-Triethylbenzene.

having an equal number of carbon atoms in the alkyl group has ever been expressed for the purpose of identifying this type of hydrocarbon. When the logarithms of relative retention for alkylbenzenes with an equal number of carbon atoms in the alkyl group were plotted against their boiling points, a straight line resulted. Fig. 2 shows five such lines corresponding to alkylbenzenes having 2, 3, 4, 5, and 6 carbon atoms in the alkyl groups. It is interesting to see that these lines are parallel to each other. There is a similar correlation at 200°.

Indans and tetralin, which have a benzene nucleus and a fused saturated ring, fall closely on the correlation curves for alkylbenzenes with the corresponding number of carbon atoms in the alkyl group and therefore are included in these series. Indenes, styrenes, and naphthalene which have a double bond in the "side chain", however, do not follow the corresponding curves and appear to have a different pattern. From the limited data obtained at present, no correlation can be found for these types.

These correlation curves can be expressed by the following empirical equation:

$$\text{Log } V_R = mT_B - c \qquad (2)$$

where V_R = relative retention of an alkyl benzene, T_B = normal boiling point of the compound, °C, m = slope, c = Y — intercept at any temperature; 0° arbitrarily selected.

The slope for the set of five alkylbenzene series at 150° on a stationary phase of Apiezon L grease is 0.0134, and their intercepts on the vertical axis at 0° are 2.0294, 2.1242, 2.1937, 2.2498, and 2.2952 for alkylbenzenes with 2, 3, 4, 5, and 6 carbon atoms in the alkyl group. The values of the intercept c are, of course, a measure of the separation of the five parallel lines from each other.

The intercept c in eqn. 2 can be correlated with the number of carbon atoms in the alkyl group, N_C, as shown in Fig. 3. This can be expressed as follows:

$$\text{Log } N_C = a \log c - b \qquad (3)$$

where N_C = number of carbon atoms in the alkyl group, a = slope, b = intercept.

For the curve shown in Fig. 3, a = 8.78 and b = 2.431.

From eqn. 3, it is possible to generate a family of relative retention–boiling-point curves when only one is known.

The relationship between relative retentions and boiling points of alkylbenzenes was found to be very useful for characterization. For example, peak 6 in the chromatogram shown in Fig. 1 has a relative retention of 2.16. By checking the curves in Fig. 2, it was readily determined that the boiling point of this unknown in a distillate fraction boiling at about 192–198° should be 189.3° if it is an alkylbenzene having four carbons in the alkyl group or 193.5° if it has an alkyl group of five carbon atoms. 1,2-Dimethyl-4-ethylbenzene boils at 189.79° and 1-methyl-3-isobutyl- and 1-methyl-3-*sec.*-butylbenzene both boil at 194°. The infrared spectrum of the collected material producing this peak agreed very well with that of 1,2-dimethyl-4-ethylbenzene.

Calibration factor (f_C) and type of aromatic hydrocarbon

An examination of the calibration factor (f_C) data in Table III disclosed that the molecular structure of the compounds plays an important role in determining the value of this factor, while within each type the variation in value is relatively small.

Referring to Table III, for all alkylbenzenes the values are 0.93–1.10, with an average of nearly 1.0; for indenes, styrenes, and naphthalene, 1.15, 1.1, and 1.14; and for indan and tetralin, 1.65 and 2.05. Considering the benzene nucleus as a common structural center for all compounds, the alkylbenzenes are obviously in one group; styrenes, indenes, and naphthalene, which all have unsaturation in the other part of the molecule, form another group; indan and tetralin, with the non-benzene part saturated and cyclic, are different from the other two groups. The difference between indan and tetralin is probably due to the number of carbon atoms in the saturated cyclic part of the molecule. It is interesting to note that benzofuran, having an unsaturated part in addition to the benzene nucleus, has a value of 1.15, quite similar to that of the second group although it contains an oxygen atom.

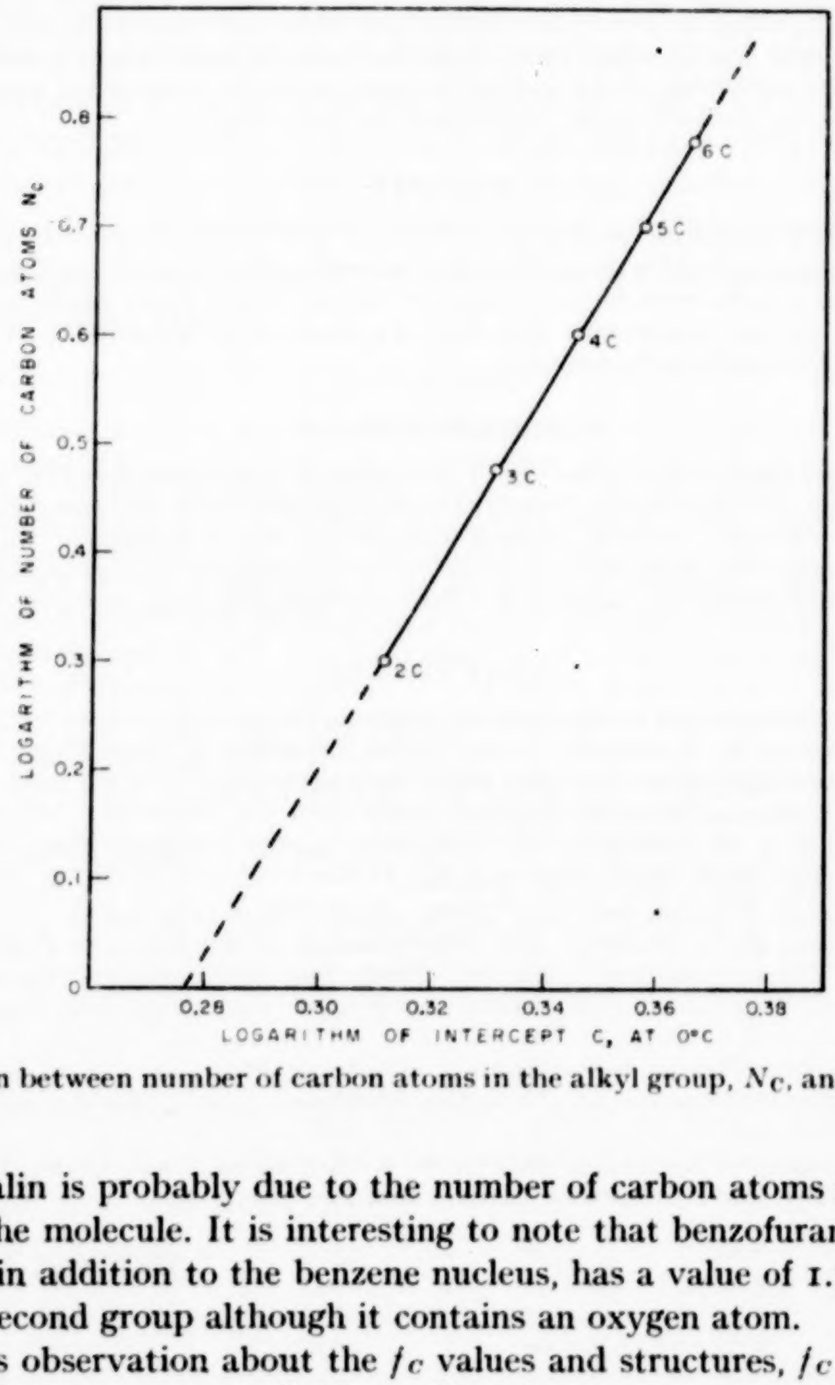

Fig. 3. Correlation between number of carbon atoms in the alkyl group, N_C, and intercept C at 0°.

Based on this observation about the f_C values and structures, f_C values for some hydrocarbons that were not available in this laboratory were assumed to be equal to those of either their isomers or of structurally similar compounds. Thus, f_C, 1.09, for 1,3-dimethyl-5-ethylbenzene was used for estimation of all dimethylethyl benzenes; 1.11 for 1-methyl-3,5-diethylbenzene for all methyldiethyl benzenes; 1.65 of indan for all methyl indans; 1.15 of benzofuran for all methyl benzofurans, and 1.00, an average value for 1,2,4,5- and 1,2,3,5-tetramethylbenzene, for 1,2,3,4-tetramethylbenzene.

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SUMMARY

52 Aromatic hydrocarbons boiling up to 218° were identified in a low-temperature bituminous coal tar by means of gas–liquid chromatography and infrared spectrophotometry, 27 of these for the first time. Quantitative determinations were made on 43 compounds boiling up to 200°. It was shown that alkylbenzenes with equal numbers of carbon atoms in their alkyl groups exhibit a linear relationship between log relative retention and normal boiling point, and that the C_8, C_9, C_{10}, C_{11}, and C_{12} alkylbenzenes lie on five parallel lines whose separation from each other is related to the logarithm of the number of carbon atoms in the alkyl group. Examples of the accuracy and utility of these novel correlations are presented.

RÉSUMÉ

Cinquante-deux hydrocarbures aromatiques (P.E. $< 218°$) dont 27 pour la première fois, ont pu être identifiés dans un goudron de houille, par chromatographie gaz–liquide et spectrophotométrie infra-rouge. Quarante-trois de ces composés ont été dosés. Cette étude a permis d'obtenir d'utiles renseignements sur la structure chimique du goudron, le mécanisme de la carbonisation et pour de nouvelles utilisations du goudron.

ZUSAMMENFASSUNG

In Tief-Temperatur Bitumenteer konnten 52 aromatische Kohlenwasserstoffe mit Siedepunkten bis zu 218° mit Hilfe der gas–flüssig Phasenchromatographie und Infrarot-Spektrophotometrie identifiziert werden, wovon 27 Verbindungen zum ersten Mal aufgefunden wurden. 43 Verbindungen wurden quantitativ bestimmt. Es konnten Gesetzmässigkeiten zwischen dem chromatographischen Verhalten (Retentionswerte), der Zahl der Kohlenstoffatome und den Siedepunkten aufgedeckt werden.

REFERENCES

[1] A. Jäger and G. Kattwinkel, *Brennstoff-Chem.*, 35 (1954) 353.

[2] G. T. Morgan and A. E. J. Pettet, *J. Soc. Dyers Colourists*, 54 (1938) 17.

[3] A. Parant, *Compt. rend. congr. ind. gaz. Paris*, 65 (1948) 409.

[4] R. Weissgerber, *Brennstoff-Chem.*, 5 (1924) 208.

[5] D. W. Grant and G. A. Vaughan, D. H. Desty, editor, *Vapour Phase Chromatography*, Academic Press, Inc., New York 1957, p. 419.

[6] C. H. Fisher and A. Eisner, *Ind. Eng. Chem., Anal. Ed.*, 9 (1937) 213.

[7] R. M. Gooding and R. L. Hopkins, *The Determination of Aromatics in Petroleum Distillates*; presented at the Chicago meeting of the Am. Chem. Soc., September 9–13, 1946.

[8] G. U. Dinneen, C. W. Bailey, J. R. Smith and John S. Ball, *Ind. Eng. Chem., Anal. Ed.*, 19 (1947) 992.

[9] D. H. Desty, *Vapour Phase Chromatography*, Academic Press, Inc., New York 1957, p. xiii.

[10] L. T. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley & Sons, Inc., New York 1956, p. 54.

[11] A. I. M. Keulemans, A. Kwantes, and G. W. A. Rijnders, *Anal. Chim. Acta*, 16 (1957) 29.

[12] D. H. Desty and B. H. F. Whyman, *Anal. Chem.*, 29 (1957) 320.

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Short Communication

Determination of traces of nickel in uranium

A rapid method was required for the determination of microgram amounts of nickel in uranium. Dimethylglyoxime in ammoniacal solution has long been used for the determination of small amounts of nickel[1,2] but none of the reported methods[2-4] is satisfactory for the direct determination of nickel in uranium. The method proposed here uses an elevated pH (11.5 ± 0.5)[5,6] in order to obtain a stable colour. This high pH could be attained without precipitation of uranium, thorium, iron, etc., by using ammonium carbonate and ammonium citrate as the complexing agent. The limit of determination is 5 μg nickel per gram of U_3O_8; this can be extended to 1 p.p.m. by using a 5-cm absorption cell.

PROCEDURE

Two 1-g samples were weighed into 100-ml beakers, dissolved in nitric acid and the solutions evaporated to dryness. The residue was taken up with 1 ml of 1:1 sulphuric acid and diluted to 20 ml with water. 2 ml of saturated bromine water were added and the solution set aside for 5 min, after which ammonia (1:1) was added dropwise to destroy the excess of bromine and to form a permanent precipitate of ammonium diuranate. 10 ml of 25% (w/v) ammonium carbonate solution and 2 ml of 25% (w/v) ammonium citrate solution were then added and the solution cooled to about 20°. 8 ml of 25% (w/v) sodium hydroxide solution were added dropwise with stirring and the pH adjusted to 11.5 ± 0.5 by addition of a few drops of sodium hydroxide solution. 2 ml of dimethylglyoxime reagent (1% in alcohol) were added to one of the beakers, the other solution serving as the reference blank. The solutions were made up to 50 ml in volumetric flasks and set aside for 30 min for full colour development. After this time, the colour was stable for at least 24 h. The absorbancy of the solution was measured on a spectrophotometer at 530 mμ and the nickel concentration determined by reference to a standard curve prepared by taking between 5 and 100 μg of nickel in the presence of 1 g of U_3O_8 and following the same procedure. 50 μg Ni in a 1-cm cell at 530 mμ showed an optical density of 0.15.

TABLE I

Interfering metal	*Amount added* μg	*Ni added* μg	*Ni found* μg
Copper(II)	50	10.0	10.0
	100	10.0	10.0
	50	30.0	30.0
	100	30.0	29.5
Cobalt(II)	50	10.0	10.0
	100	10.0	11.5
	50	30.0	30.0
	100	30.0	31.5
Chromium(III)	50	10.0	10.0
	100	10.0	11.5
	50	30.0	30.0
	100	30.0	31.0

Copper(II), cobalt(II), and chromium(III) are the only interfering metals but their colours with dimethylglyoxime are much weaker than the nickel colour[1]; the

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effects of these elements are shown in Table 1. No interference occurs if the amounts in the sample aliquot are 50 μg or less; the interference is slight if the amount of the interfering metal is 100 μg.

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[1] E. B. Sandell, *Colorimetric Determination of Traces of Metals,* Interscience Publishers, New York 1950, p. 470.

[2] C. J. Rodden, *Analytical Chemistry of the Manhattan Project,* McGraw Hill Book Co., New York 1950, p. 434.

[3] L. G. Bassett, D. J. Pflaum, R. J. Rutman, C. J. Rodden and N. H. Furman, *U.S., A.E.C., Report,* A2912, Vol. III, 1946.

[4] N. H. Furman, G. P. Haight, Jr. and B. McDuffie, *U.S., A.E.C., Report,* No. M4249 1955, *U.S., A.E.C. Report,* M2783 1956.

[5] A. T. Blackwell, A. M. Daniel and J. D. Miller, *Anal. Chem.,* 28 (1956) 1209.

[6] K. Yamasaki and C. Matsumoto, *J. Chem. Soc. Japan, Pure Chem. Sect.,* 78 (6) (1957) 833; *Anal. Abstr.,* 5 (4) (1958) 1231.

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REVUES DE LIVRE

Source material for radiochemistry – Nuclear science series – Report number 27 – Subcommittee on radiochemistry – Committee on nuclear science – Publication number 654, National Academy of Science, National Research Council, Washington D.C., mars 1959.

Il est fort difficile d'obtenir des renseignements précis et complets sur la bibliographie concernant la radiochimie. Le sous-Comité en radiochimie a comblé cette lacune. Dans son No. de mars 1959, il donne une liste de 60 références (primarly documents) avec, en quelques lignes, l'objet de celles-ci et, initiative heureuse, l'adresse exacte permettant de se procurer l'ouvrage désiré.

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Papierchromatographie, Heft 2, et *Ionenaustauscher* par Dr. Herbert Daecke. Otto Salle Verlag, Frankfurt, Hamburg, 1959, 43 p. DM. 3.80.

Ces opuscules font partie de la collection Schriffenreiche zur Chemie. L'auteur y expose, en quelques pages, les principes essentiels, les applications et le mode opératoire de la séparation chromatographique sur papier et des échangeurs d'ions. Présentation claire, très simplifiée qui convient particulièrement bien à tous ceux qui désirent s'initier à ces remarquables techniques de séparation, parmi les plus importantes de l'analyse chimique moderne. Une bibliographie sommaire, mais soigneusement choisie donne le titre des principaux traités généraux parus dans le domaine de la chromatographie et des échangeurs d'ions ainsi qu'un certain nombre de monographies et d'ouvrages plus particulièrement axés sur le mode opératoire.

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SOME THEORETICAL CONSIDERATIONS IN ANALYTICAL CHEMISTRY

II[1]. DISCRIMINANTS IN ION COMBINATION REACTION CALCULATIONS

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In the calculation of ion concentrations in ion combination reactions, *e.g.* in titrimetry, there is often presented a choice of equations of differing precision or exactness[2]. For example, in calculating the equivalence point pH in the titration of a weak base with a strong acid, if the ionisation of the solvent and the loss of cation by hydrolysis can both be ignored, a crude equation, the *simple* form (1), is employed,

$$[\mathrm{H}^+] = \left(\frac{cK_w}{K_b}\right)^{\frac{1}{2}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

When the ionisation of the solvent is taken into account, but hydrolysis is ignored, one *approximate* form (2) which incorporates the solvent ionisation correction is applied,

$$[\mathrm{H}^+] = \left(\frac{cK_w}{K_b} + K_w\right)^{\frac{1}{2}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

When, contrariwise, the loss of cation is taken into account, but the ionisation of the solvent is ignored, another *approximate* form (3), corrected for hydrolysis, is required,

$$[\mathrm{H}^+] = \frac{1}{2K_b}\left\{(K_w^2 + 4K_wK_bc)^{\frac{1}{2}} - K_w\right\} \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Though these two corrections normally tend to be mutually exclusive, and the approximate equations are more nearly precise than the simple form, neither is yet entirely precise, and under certain conditions an *exact* form (4) is called into use which incorporates all the corrections and is exact under all conditions,

$$K_b a_{\mathrm{H}^+}^3 + K_w a_{\mathrm{H}^+}^2 - (K_bK_w + a_cK_w)a_{\mathrm{H}^+} + K_w^2 = 0 \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

or, writing concentrations instead of active masses,

$$K_b[\mathrm{H}^+]^3 + K_w[\mathrm{H}^+]^2 - (K_bK_w + cK_w)[\mathrm{H}^+] + K_w^2 = 0 \; . \; . \; . \; . \; . \; . \; . \quad (4a)$$

Strictly, activities should be used in all the equations, but this does not alter the order of the equations.

In moving from the simple through the various approximate forms to the exact form, the order of the equations increases. With simple symmetrical binary compounds the movement is from a linear to various quadratics to a cubic equation. The labour and difficulty of solving these equations rises rapidly with increasing exactness of the solutions, so it is desirable to use the simplest possible equation compatible with the required accuracy of the solution.

The error

In making calculations, the analyst has in mind a certain permissible error, which is set either by the precision required from the practical determination, or by the known precision of the measurements made in the course of the determination. For instance, if pH is the quantity concerned and the experimental technique permits of discrimination to ± 0.01 pH unit, the precision would be roughly 2% on the hydrogen ion concentration. This would then be the permissible error in the calculations, though it is customary to calculate to a slightly higher precision, so 1% would probably be chosen. The relative error incurred in using a less precise equation (giving a value Q_1) instead of a more precise equation (giving a value Q_2) in the calculation is given by

$$E = \pm \frac{Q_1 - Q_2}{Q_2} \quad \ldots\ldots\ldots\ldots \quad (5)$$

Examination of the correction incorporated in the more precise equation will determine which sign should be employed to give E a positive value. Multiplication of E by 100 gives the percentage error.

The question now arises of deciding if and when it is necessary to change over from one equation to a more precise equation. To do this by trial and error can be as tedious as using the more precise equation throughout the whole series of calculations. Some simple means is needed of delineating the exact conditions under which the change over one way or the other is required. This decision may be placed on a simple quantitative basis by the use of expressions which discriminate between the alternative equations for a specified permissible error. For these discriminating expressions, the term *discriminant** is proposed.

Derivation of discriminants

The exact conditions under which the change from one equation to another should be made for a specific error can readily be defined by substituting the appropriate values in (5), simplifying to a *master discriminant*, and solving this equation for the particular condition in question, giving a series of *particular discriminants*. In the case quoted above, to decide when correction for ionisation of the solvent is necessary, substitution in (5) of the values for $[\mathrm{H}^+]$ from (1) and (2) (which is the greater) gives.

$$\frac{\left(c\dfrac{K_w}{K_b} + K_w\right)^{\frac{1}{2}} - \left(c\dfrac{K_w}{K_b}\right)^{\frac{1}{2}}}{\left(c\dfrac{K_w}{K_b} + K_w\right)^{\frac{1}{2}}} = E \quad \ldots\ldots\ldots\ldots \quad (6)$$

Simplification of (6) gives the *master discriminant* (7),

$$cE(2 - E) - K_b(1 - E)^2 = 0 \quad \ldots\ldots\ldots\ldots \quad (7)$$

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* The term is here used as an abbreviation for "discriminating expression", and should not be confused with the mathematical use of the term in the treatment of complex quantities.

which can be solved for E, c or K_b as required, and shows that the simple equation (1) is adequate when

$$c \geqslant \frac{K_b(1 + E)^2}{E(2 - E)} \approx \frac{K_b}{2E} \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

or when

$$K_b \leqslant \frac{E(2 - E)c}{(1 + E)^2} \approx 2Ec \quad \ldots\ldots\ldots\ldots\ldots \quad (9)$$

These expressions are then the *particular discriminants*, (9), for example, being the base ionisation constant discriminant for solvent ionisation correction, indicating that if the ionisation constant of the base exceeds the given value, ignoring the ionisation of the solvent will incur an error greater than that stipulated.

A further use of discriminants is in the assessment or calculation of errors incurred by ignoring particular corrections[3], by solving the master discriminant for the term E, as in equations (26), (34), (43) and (48).

The multiplicity of equilibria involved in titrimetric and other analytical calculations makes complete coverage too lengthy. The purpose of the following account is to give sufficient examples to permit direct treatment of the commoner calculations by means of discriminants, and to provide a pattern for the derivation of discriminating expressions wherever alternative equations of differing precision present themselves. For the classification of titrimetric processes, the utility and application of the various calculations and the derivation of the simple, approximate and exact equations, reference should be made to the standard texts[2]. For brevity in the following account, the arguments and the algebraic working have been omitted.

1. *Discriminants in hydrogen ion concentration calculations*

(*a*) *Weak acids.* For a solution of molar concentration c of an acid of ionisation constant K_a,

$$\text{Simple } [\mathrm{H^+}] = (K_a c)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

$$\text{Exact } [\mathrm{H^+}] = {}^1/_2\{K_a + (K_a^2 + 4K_a c)^{\frac{1}{2}}\} \quad \ldots\ldots\ldots\ldots \quad (11)$$

Substitution in (5) and simplification gives the *master discriminant*,

$$cE^2(2 + E)^2 - K_a(1 + E)^2 = 0 \quad \ldots\ldots\ldots\ldots \quad (12)$$

Solution of which gives the particular discriminants (13) and (14) which indicate that the simple form (10) is sufficiently accurate when

$$c \geqslant K_a\left(\frac{(1 + E)}{E(2 + E)}\right)^2 \approx \frac{K_a}{4E^2} \quad \ldots\ldots\ldots\ldots \quad (13)$$

or

$$K_a \leqslant c\left(\frac{E(2 + E)}{(1 + E)}\right)^2 \approx 4E^2c \quad \ldots\ldots\ldots\ldots \quad (14)$$

(*b*) *Weak bases.* Although the simple and exact forms for [H+] are different from those for weak acids[2], the discriminants are the same, and substitution of K_b for K_a in (12), (13) and (14) gives the discriminants for weak bases.

(*c*) *Hydrolyzed salt solutions. Salts of weak bases with strong acids.* When the ionisation constant of the weak base is K_b and the concentration of the salt is c, equations (1) to (4) apply. Discriminants for ionisation of the solvent (7) to (9) have already been derived.

When loss of cation by hydrolysis must be taken into account, substitution of (1) and (3) in (5) yields the *master discriminant* for the hydrolysis correction,

$$E^2(2 + E)^2cK_b - (1 + E)^2K_w = 0 \quad \ldots \quad (15)$$

The *particular discriminants* (16) and (17) show that the simple form (1) is valid when

$$K_b \gg \left(\frac{1 + E}{E(2 + E)}\right)^2 \frac{K_w}{c} \approx \frac{K_w}{4E^2c} \quad \ldots \quad (16)$$

or when

$$c \gg \left(\frac{1 + E}{E(2 + E)}\right)^2 \frac{K_w}{K_b} \approx \frac{K_w}{4E^2K_b} \quad \ldots \quad (17)$$

Salts of weak acids with strong bases. Despite the fact that simple, approximate and exact forms are different[2], the discriminants are the same as for salts of weak bases with strong acids, and substitution of K_a for K_b in (7), (8), (9), (15), (16) and (17) yields the appropriate discriminants.

Hydrolyzed salts in the presence of a small excess of strong acid or base. If the untitrated or excess of strong acid in the titration of a weak base is calculated from reagent strength and solution volume to be c_a, the concentration of the salt is c_s and the ionisation constant of the base is K_b, then

$$\text{Simple } [\mathrm{H^+}] = c_a \quad \ldots \quad (18)$$

$$\text{Exact } [\mathrm{H^+}] = {}^1/_2\left\{\left(c_a^2 + \frac{4K_wc_s)}{K_b}\right)^{\frac{1}{2}} + c_a\right\} \quad \ldots \quad (19)$$

Substitution of (18) and (19) in (5) yields the discriminant (20) which shows that the simple value c_a gives sufficiently accurate results when

$$c_a \gg (1 - E)\left\{\frac{K_w c_s}{K_bE}\right\}^{\frac{1}{2}} \quad \ldots \quad (20)$$

that is, when there is sufficient strong acid present adequately to suppress hydrolysis of the salt.

Substitution of c_b and K_a in (20) gives the discriminant for free strong base concentration in the titration of a weak acid with a strong base.

(*d*) *Acid buffer solutions.* For a weak acid of ionisation constant K_a and concentration c_a in mixture with a concentration c_s of its salt with a strong base, when ionisation of the acid and hydrolysis of the salt are both adequately suppressed,

$$\text{Simple } [\mathrm{H^+}] = \frac{c_a}{c_s} K_a \quad \ldots \quad (21)$$

When ionisation of the acid is not adequately suppressed, but hydrolysis can be ignored,

$$\text{Approx. } [\mathrm{H^+}] = {}^1/_2\left[\left\{(c_s + K_a)^2 + 4K_ac_a\right\}^{\frac{1}{2}} - (c_s + K_a)\right] \quad \ldots \quad (22)$$

When hydrolysis of the salt is taken into account, but ionisation of the acid can be ignored,

$$\text{Approx. } [\mathrm{H^+}] = \frac{1}{2c_s}\left[\left\{(c_aK_a + K_w)^2 + 4K_aK_wc_s\right\}^{\frac{1}{2}} + (K_w + c_aK_a)\right] \quad \ldots \quad (23)$$

Though these two corrections are usually in opposition, they are not mutually exclusive, and in the rare cases when both ionisation of the acid and hydrolysis of the salt must be accounted for, the exact equation (24) is required.

$$\text{Exact } [\mathrm{H^+}]^3 + (c_s + K_a)[\mathrm{H^+}]^2 - (K_w + K_ac_a)[\mathrm{H^+}] - K_aK_w = 0 \quad \ldots \quad (24)$$

Correction for ionisation of the weak acid. Substitution of (21) and (22) in (5) and simplification yields the *master discriminant* (25)

$$c_aK_a + c_sK_a(1 + E) - Ec_s^2(1 + E) = 0 \tag{25}$$

This carries four possible variables, E, c_a, c_s and K_a, and may be solved for the error incurred under any given conditions by (26),

$$E = \frac{1}{2c_s}\left[\left\{(c_s - K_a)^2 + 4K_a(c_a + c_s)\right\}^{\frac{1}{2}} - (c_s - K_a)\right] \tag{26}$$

or may be sorted to give *particular discriminants* (27) to (29) for the variable of interest. These indicate that the simple form (21) is valid when

$$c_s \geqslant \frac{1}{2E}\left[\left\{K_a^2 + \frac{4EK_ac_a}{1 + E}\right\}^{\frac{1}{2}} + K_a\right] \approx \left(\frac{c_aK_a}{E}\right)^{\frac{1}{2}} \tag{27}$$

$$c_a \leqslant \frac{c_s(1 + E)(Ec_s - K_a)}{K_a} \approx \frac{Ec_s^2}{K_a} \tag{28}$$

$$K_a \leqslant \frac{c_s^2E(1 + E)}{c_a + (1 + E)c_s} \approx \frac{Ec_s^2}{c_a} \tag{29}$$

The conditional approximations of (27) to (29) apply when c_a is large compared with $[H^+]$ and c_s, and like those in (8), (9), (13), (14), (16) and (17) must be used with caution.

Since the term c_a/c_s appears in (21), it is often convenient to work in terms of this ratio, denoted by the symbol n, when particular discriminants become, in favour of the corrected expression (22),

$$n \geqslant \frac{(1 + E)(Ec_s - K_a)}{K_a} \geqslant \frac{1 + E}{2}\left[\left\{1 + \frac{4Ec_a}{(1 + E)K_a}\right\}^{\frac{1}{2}} - 1\right] \tag{30}$$

$$c_s \leqslant \frac{K_a(1 + E + n)}{E(1 + E)} \tag{31}$$

$$c_a \geqslant \frac{nK_a(1 + E + n)}{E(1 + E)} \tag{32}$$

A corresponding set of discriminants for the reciprocal of this ratio is also of occasional use.

Correction for hydrolysis of the salt. Substitution of (21) and (23) in (5) and simplification yields the *master discriminant* (33),

$$(1 - E)^2c_sK_w + (1 - E)c_aK_w - Ec_a^2K_a = 0 \tag{33}$$

Solution for the error gives, in the most convenient form for series of calculations,

$$E = {}^1/_2\left[\left(\frac{K_ac_a^2}{K_wc_s} + \frac{c_a}{c_s} + 2\right) - \left\{\left(\frac{K_ac_a^2}{K_wc_s} + \frac{c_a}{c_s} + 2\right)^2 - \frac{4(c_a + c_s)}{c_s}\right\}^{\frac{1}{2}}\right] \tag{34}$$

Particular discriminants derived from (33) show that the simple form (21) is valid for a specified error when

$$c_a \geqslant \frac{(1 - E)}{2EK_a}\left[K_w + \left\{K_w^2 + 4EK_aK_wc_s\right\}^{\frac{1}{2}}\right] \tag{35}$$

$$c_s \leqslant \frac{c_a}{(1 - E)}\left(\frac{EK_ac_a}{(1 - E)K_w} - 1\right) \tag{36}$$

$$K_a \geqslant \frac{(1 - E)}{E}\frac{K_w}{c_a}\left\{1 + (1 - E)\frac{c_s}{c_a}\right\} \tag{37}$$

Other discriminants in terms of $n = c_a/c_s$ or $n' = c_s/c_a$ can be derived and are often useful.

(*e*) *Basic buffer solutions.* When the concentration of weak base of ionisation constant K_b is c_b and the concentration of the salt with a strong acid is c_s, then equations of differing exactness are offered, in analogy to acid buffers.

$$\text{Simple } [\mathrm{H}^+] = \frac{c_s}{c_b}\,\frac{K_w}{K_b} \quad \ldots\ldots \quad (38)$$

Correction for ionisation of the weak base gives

$$\text{Approx. } [\mathrm{H}^+] = \frac{K_w}{2K_b c_b}\left[(K_b + c_s) + \left\{(K_b + c_b)^2 + 4K_b c_b\right\}^{\frac{1}{2}}\right] \quad \ldots\ldots \quad (39)$$

Correction for hydrolysis of the salt gives

$$\text{Approx. } [\mathrm{H}^+] = \frac{1}{2K_b}\left[\left\{(K_b c_b + K_w)^2 + 4K_w K_b c_s\right\}^{\frac{1}{2}} - (K_b c_b + K_w)\right] \quad \ldots\ldots \quad (40)$$

Correction for both ionisation of the weak base and hydrolysis of the salt gives

$$\text{Exact } K_b[\mathrm{H}^+]^3 + (c_b K_b + K_w)[\mathrm{H}^+]^2 - K_w(c_s + K_b)[\mathrm{H}^+] - K_w^2 = 0. \quad \ldots \quad (41)$$

Correction for ionisation of the weak base. Substitution of (38) and (39) in (5) and simplification yields the *master discriminant* (42)

$$Ec_s^2 - (1 - E)K_b c_s - (1 - E)^2 c_b K_b = 0 \quad \ldots\ldots \quad (42)$$

from which the error incurred in the use of (38) is, in the most convenient form involving the ratio c_s/c_b,

$$E = {}^1\!/_2 \left[\left(\frac{c_s}{c_b}(\frac{c_s}{K_b} + 1) + 2\right) - \left\{\left(\frac{c_s}{c_b}(\frac{c_s}{K_b} + 1) + 2\right)^2 - 4\left(\frac{c_s}{c_b} + 1\right)\right\}^{\frac{1}{2}}\right] \quad \ldots\ldots \quad (43)$$

From (42), *particular discriminants* may be derived showing that the simple form is valid when

$$c_b \leqslant \frac{Ec_s^2 - (1 - E)K_b c_s}{(1 - E)^2 K_b} \quad \ldots\ldots \quad (44)$$

$$c_s \geqslant \frac{(1 - E)K_b}{2E}\left\{1 + \left(1 + 4E\frac{c_b}{K_b}\right)^{\frac{1}{2}}\right\} \quad \ldots\ldots \quad (45)$$

$$K_b \leqslant \frac{Ec_s^2}{(1 - E)(c_s + (1 - E)c_b)} \quad \ldots\ldots \quad (46)$$

Correction for hydrolysis of the salt. Substitution of (38) and (40) in (5) and simplification gives the *master discriminant* (47),

$$E(1 + E)K_b c_b^2 - (1 + E)K_w c_b - c_s K_w = 0 \quad \ldots\ldots \quad (47)$$

from which the error incurred in using the simple form (38) is, in the most convenient form for calculation,

$$E = {}^1\!/_2\left[\left\{\left(1 - \frac{K_w}{K_b c_b^2}\right)^2 + \frac{4K_w}{K_b c_b^2}(c_b + c_s)\right\}^{\frac{1}{2}} - \left(1 - \frac{K_w}{K_b c_b^2}\right)\right] \quad \ldots\ldots \quad (48)$$

and solution for *particular discriminants* (49) to (51) indicates that the simple form (38) is valid when

$$c_b \geqslant \frac{K_w}{2EK_b}\left[1 + \left\{1 + \frac{4EK_b c_s}{(1 + E)K_w}\right\}^{\frac{1}{2}}\right] \quad \ldots\ldots \quad (49)$$

$$c_s \leqslant \frac{(1 + E)c_b(EK_b c_b - K_w)}{K_w} \quad \ldots\ldots \quad (50)$$

$$K_b \geqslant \frac{K_w[(1 + E)c_b + c_s]}{E(1 + E)c_b^2} \quad \ldots\ldots \quad (51)$$

As before, the master discriminants may be converted into terms of the ratio $c_a/c_b = n$, or its reciprocal, and the new master discriminants solved for particular discriminants.

2. *Discriminants in precipitation reaction calculations*

(*a*) *Simple binary precipitates.* With a simple binary compound BA of solubility product S_{BA}, if one ion, say B^+, is in excess to an amount calculated from reagent concentration and volume of titration solution to be c, then the ion concentrations are

$$\text{Simple } [B^+] = c; \quad [A^-] = \frac{S_{BA}}{c} \quad \dots\dots\dots\dots \quad (52)$$

Near the equivalence point the contribution of ions from the precipitate can no longer be neglected and the concentrations become,

$$\text{Exact } [B^+] = {}^1/_2\, \{(c^2 + 4S_{BA}) + c\} \quad \dots\dots\dots\dots \quad (53)$$

$$\text{Exact } [A^-] = {}^1/_2\, \{(c^2 + 4S_{BA}) - c\} \quad \dots\dots\dots\dots \quad (54)$$

Substitution of (52) and either (53) or (54) as appropriate in (5) results in the same discriminant, since the precipitate is symmetrical, whether A^- or B^+ is in excess, and demonstrates the validity of the simple form (52) when

$$c \geqslant \left(\frac{S_{BA}}{E(1 + E)}\right)^{\frac{1}{2}} \quad \dots\dots\dots\dots \quad (55)$$

(*b*) *Binary precipitates of the first order of asymmetry.* Taking as an example the precipitate B_2A, since the precipitate is unsymmetrical, the equations will be unsymmetrical and different depending on which ion is in excess.

Anion in excess. Suppose the anion is in excess to an amount calculated to be c_A. The ion concentrations are then

$$\text{Simple } [A^{-2}] = c_A; \quad [B^+] = \left(\frac{S_{B_2A}}{c_A}\right)^{\frac{1}{2}} \quad \dots\dots\dots\dots \quad (56)$$

Near the equivalence point account must be taken of the contribution of ions from the precipitate and the concentrations become

$$\text{Exact } [A^{-2}] = c_A + {}^1/_2[B^+] \quad \dots\dots\dots\dots \quad (57)$$

$$\text{Exact } [B^+]^3 + 2c_A[B^+]^2 - 2S_{B_2A} = 0 \quad \dots\dots\dots\dots \quad (58)$$

Substitution of the values of $[A^{-2}]$ from (56) and (57) in (5) yields the discriminant (59)

$$c_A = \frac{(1 - 2E)}{2E}\,[B^+] \quad \dots\dots\dots\dots \quad (59)$$

which is impracticable. Solution of (56) for $[B^+]$ makes the assumption that $[A^{-2}] = c_A$, and will give a high value for $[B^+]$ while A^{-2} is in excess. Use of this value would mean that a change to the exact equation would be made while the error was still very slightly less than E. It is therefore safe to use this value in defining the limiting value of c_A, especially since it defines the point at which the difference between c_A and $[A^{-2}]$ becomes less than that which causes a relative error of E. Substitution of this value then gives the discriminant (60) which shows that the simple forms (56) are valid when

$$c_A \geqslant \left\{\left(\frac{1 - 2E}{2E}\right)^2 S_{B_2A}\right\}^{\frac{1}{3}} \quad \dots\dots\dots\dots \quad (60)$$

Cation in excess. If the calculated excess is c_B,

$$\text{Simple } [B^+] = c_B; \quad [A^{-2}] = \frac{S_{B_2A}}{c_B{}^2} \qquad (61)$$

$$\text{Exact } [B^+] = c_B + 2[A^{-2}] \qquad (62)$$

$$\text{Exact } 4[A^{-2}]^3 + 4c_B[A^{-2}]^2 + c_B{}^2[A^{-2}] - S_{B_2A} = 0 \qquad (63)$$

A similar process to that above, allowing $[B^+] = c_B$ at the critical point, yields the discriminant (64) which shows that the simple forms (61) are valid when

$$c_B \geqslant \left(\frac{2(1 - E)}{E} S_{B_2A}\right)^{\frac{1}{3}} \qquad (64)$$

(*c*) *Simple binary precipitates which are salts of a monobasic weak acid.* In the case of the salt BA of the weak acid HA and the base BOH where $K_b \gg K_a$, the equations will be unsymmetrical and will differ according to which ion is in excess.

Anion in excess. If the calculated excess is c_A, then remote from the equivalence point,

$$\text{Simple } [A^-] = c_A; \; [B^+] = \frac{S_{BA}}{c_A} \qquad (65)$$

Nearer the equivalence point the removal of A^- ions as unionized HA and the contribution of A^- ions from solution of the precipitate become significant,

$$\text{Exact } [A^-] = \frac{1}{2[K_a + [H^+]]}\left[c_a K_a + \left\{c_a{}^2 K_a{}^2 + 4K_a S_{BA}(K_a + [H^+])\right\}^{\frac{1}{2}}\right] \qquad (66)$$

Assuming $[A^-]$ to be greater than c_A, substitution of (65) and (66) in (5) gives the discriminant (67) which shows that the simple forms of (65) are valid when

$$c_A \geqslant (1 - E) \left\{\frac{K_a S_{BA}}{[H^+] + EK_a}\right\}^{\frac{1}{2}} \qquad (67)$$

Cation in excess. For a calculated excess of c_B,

$$\text{Simple } [B^+] = c_B; \quad [A^-] = \frac{S_{BA}}{c_B} \qquad (68)$$

$$\text{Exact } [B^+] = {}^1/_2\left[c_B + \left\{c_B{}^2 + 4S_{BA}\left(1 + \frac{[H^+]}{K_a}\right)\right\}^{\frac{1}{2}}\right] \qquad (69)$$

From (68) and (69) the discriminant (70) may be derived showing the validity of (68) when

$$c_B \geqslant \left\{\frac{(1 - E)}{E} S_{BA}\left(1 + \frac{[H^+]}{K_a}\right)\right\}^{\frac{1}{2}} \qquad (70)$$

3. *Discriminants in complexation reaction calculations*

(*a*) *Simple symmetrical 1:1 complexes not involving the production of hydrogen ion.* In the case of a complex ML of instability constant K_{inst} present in concentration c, if the calculated excess of one ion be c_L or c_M as appropriate, the concentration of the other ion will be

$$\text{Simple } [M] = \frac{c\;K_{inst}}{c_L} \qquad (71)$$

$$\text{Simple } [L] = \frac{c\;K_{inst}}{c_M} \qquad (72)$$

Close to the equivalence point, if M is in excess, the true state of affairs is

$$\text{Exact } [\mathrm{L}] = {}^1/_2[\{(c_{\mathrm{M}} + K_{inst})^2 + 4c\, K_{inst}\}^{\frac{1}{2}} - (c_{\mathrm{M}} + K_{inst})] \quad . \; . \; . \; . \quad (73)$$

$$\text{Exact } [\mathrm{M}] = {}^1/_2[\{(c_{\mathrm{M}} + K_{inst})^2 + 4c\, K_{inst}\}^{\frac{1}{2}} + (c_{\mathrm{M}} + K_{inst})] \quad . \; . \; . \; . \quad (74)$$

Substitution of (72) and (73) in (5) followed by simplification gives the *master discriminant* (75).

$$E\, c_{\mathrm{M}}^2 + E(1 - E)K_{inst}\, c_{\mathrm{M}} - (1 - E)^2 c\, K_{inst} = 0 \; . \; . \; . \; . \; . \; . \; . \; . \quad (75)$$

Solution of (75) gives *particular discriminants* of which the most important is (76) showing that (72) is valid when

$$c_{\mathrm{M}} \geqslant \frac{(1 - E)}{2}\left[\left\{K_{inst}^2 + \frac{4c\;K_{inst}}{E}\right\}^{\frac{1}{2}} - K_{inst}\right] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (76)$$

Since the complex is symmetrical, substitution of c_{L} for c_{M} in the expressions above gives the appropriate equations when L is in excess.

(*b*) *Complexes of the first order of asymmetry, such as* BA_2^-. If one or other of the ions is present in excess, calculated to be c_{A} or c_{B}, sufficient adequately to suppress dissociation of the complex, whose calculated concentration is c, then ion concentrations can be calculated from the instability constant,

$$\text{Simple } [\mathrm{A}^-] = \left(\frac{c\;K_{inst}}{c_{\mathrm{B}}}\right)^{\frac{1}{2}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (77)$$

$$\text{Simple } [\mathrm{B}^+] = \frac{c\;K_{inst}}{c_{\mathrm{A}}^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (78)$$

Close to the equivalence point, dissociation of the complex becomes significant, and expressions which differ according to which ion is in excess are required.

Cation in excess. The true concentrations are now obtained from

$$\text{Exact } [\mathrm{B}^+] = c_{\mathrm{B}} + {}^1/_2[\mathrm{A}^-] \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (79)$$

$$\text{Exact } [\mathrm{BA_2}^-] = c - {}^1/_2[\mathrm{A}^-] \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (80)$$

$$\text{Exact } [\mathrm{A}^-]^3 + 2c_{\mathrm{B}}[\mathrm{A}^-]^2 + K_{inst}[\mathrm{A}^-] - 2c\, K_{inst} = 0 \; . \; . \; . \; . \; . \; . \; . \quad (81)$$

To derive a discriminant from (77) and (81) is impracticable, but as in the derivation of (60), the use of (79) and the simple value c_{B} yields a safe working equation. Substitution of (79) and c_{B} in (5) gives

$$2Ec_{\mathrm{B}} = (1 - E)[\mathrm{A}^-] \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (82)$$

Solution of (77) for $[\mathrm{A}^-]$ gives a slightly low value, which is usable as it defines the point at which substitution of c_{B} for $[\mathrm{B}^+]$ incurs a relative error of E. Substitution of this value in (82) gives the *particular discriminant* of immediate interest which shows that (77) gives valid results when

$$c_{\mathrm{B}} \geqslant \left\{\left(\frac{1 - E}{2E}\right)^2 c\;K_{inst}\right\}^{\frac{1}{3}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (83)$$

Anion in excess. The true concentrations are now derived from

$$\text{Exact } [\mathrm{A}^-] = c_{\mathrm{A}} + 2[\mathrm{B}^+] \; . \quad (84)$$

$$\text{Exact } [\mathrm{BA_2}^-] = c - 2[\mathrm{B}^+] \; . \quad (85)$$

$$\text{Exact } 4[\mathrm{B}^+]^3 + 4c_{\mathrm{A}}[\mathrm{B}^+]^2 + (c_{\mathrm{A}}^2 + K_{inst})[\mathrm{B}^+] - c\, K_{inst} = 0 \; . \; . \; . \; . \; . \quad (86)$$

From the simple value c_{A} and (84), and substituting the value of $[\mathrm{B}^+]$ from (78), the *particular discriminant* (87) emerges, showing that the simple form (78) is valid when

$$c_{\mathrm{A}} \geqslant \left(\frac{2(1 - E)}{E}\, c\;K_{inst}\right)^{\frac{1}{3}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (87)$$

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SUMMARY

The use of discriminating expressions, termed *discriminants*, is proposed to place on a simple quantitative basis the selection of the appropriate equation for an analytical calculation for which alternative equations of differing degrees of exactitude present themselves. Sufficient examples of discriminants are given to permit direct treatment of the commoner calculations in titrimetric analysis, and to afford a pattern for their derivation whenever a choice of alternative equations is offered.

RÉSUMÉ

Des formules mathématiques („discriminants") sont proposées, permettant de choisir, sur une base quantitative, l'équation qui convient le mieux pour un calcul analytique lorsque plusieurs de ces équations, mais de degré de précision différent, existent. Des exemples sont donnés pour permettre d'effectuer directement les calculs les plus courants de l'analyse volumétrique.

ZUSAMMENFASSUNG

Es wird die Verwendung von „Diskriminanten" vorgeschlagen, um aus verschieden möglichen approximativen Gleichungen für analytische Berechnungen mit streuender Genauigkeit die geeignete Gleichung auszuwählen. Es werden verschiedene Beispiele für Diskriminanten angeführt, die eine direkte Durchführung der üblichen Berechnungen titrimetrischer Analysen gestatten.

REFERENCES

[1] E. BISHOP, *Anal. Chim. Acta*, 7 (1952) 15.
[2] E. BISHOP, *Theory and Principles of Titrimetric Analysis*, Volume I, Part B of *Comprehensive Analytical Chemistry*, Elsevier, Amsterdam 1959.
[3] E. BISHOP, *Anal. Chim. Acta*, in the press.

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SEPARATIONS INVOLVING SULPHIDES

XI. SEPARATION OF ALUMINIUM OR URANIUM FROM SOME ELEMENTS FORMING THIOSALTS

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The present investigation deals with the separation of aluminium or uranium from the elements which are estimated by decomposing their thiosalts with hydrochloric acid. The general method adopted was to treat the solution containing the two metals with sodium sulphide reagent and hydrochloric acid. The sulphide was filtered and weighed, and aluminium or uranium in the filtrate was estimated as oxinate. The separation of arsenic, antimony, tellurium, selenium, molybdenum, mercury, gold, platinum or rhenium from aluminium or uranium was studied.

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EXPERIMENTAL

Standard solutions of sodium arsenate, potassium antimony tartrate, potassium pyroantimonate, potassium tellurite, selenious acid, ammonium molybdate, mercuric chloride, gold chloride, platinum chloride, potassium perrhenate, potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ (containing a little sulphuric acid) and uranyl acetate were used. Measured volumes of the two solutions were mixed and the mixture was treated with 2 *N* sodium sulphide reagent in excess. The mixture containing the thiosalt was acidified with a measured quantity of hydrochloric acid, heated to boiling and allowed to cool to room temperature. The precipitated sulphide was filtered through a sintered glass crucible (porosity 4) and weighed as As_2S_5[1], Sb_2S_3[2], Sb_2S_5[3], TeS_2[1], SeS_2[1], $MoS_3 \cdot 2H_2O$[4], HgS[5], Au_2S_3[2], $PtS_2 \cdot 3H_2O$[3], or Re_2S_7[5].

The following points should be noted in precipitating the sulphides.

1. In the case of aluminium, the solution of potassium antimony tartrate should not be used, as tartrate interferes in the estimation of aluminium as oxinate.

2. With antimonate, the free acid of potash alum should be neutralized before antimonate is added, to avoid the precipitation of antimonic acid. In other cases the neutralization with caustic soda can be done after mixing the two solutions.

3. With uranium, any precipitate which appears on mixing the two solutions need not be dissolved in acid.

4. In the case of mercury, the mixture should be treated with ammonium hydroxide before sodium sulphide reagent is added.

5. For arsenic, platinum or rhenium, the final acidity should be 6 *N*, for selenium 2 *N* and for the other elements 1 *N*.

6. After acidification the mixture should be treated with 10–15 g of ammonium acetate for platinum and with 10–15 g of ammonium sulphate for rhenium.

7. In filtering rhenium heptasulphide the suction should be slow.

After the sulphide had been filtered, the filtrate was evaporated to about 50 ml to remove hydrogen sulphide and aluminium[6] or uranium[7] was estimated as oxinate. 36–46 mg of arsenic were separated from 10–12 mg of aluminium, 38–39 mg of antimony were separated from 10–12 mg of aluminium, 44–55 mg of tellurium were separated from 10–13 mg of aluminium, 44–52 mg of selenium were separated from 10–23 mg of aluminium, 62–73 mg of molybdenum were separated from 10–12 mg of aluminium, 68–85 mg of mercury were separated from 10–13 mg of aluminium, 12–23 mg of gold were separated from 13–23 mg of aluminium, 34–45 mg of platinum were separated from 10–12 mg of aluminium, 31–38 mg of rhenium were separated from 10–12 mg of aluminium.

The metals were recovered with an accuracy of:

As: —0.27% to 0.0%, Al: 0.0% to + 0.36%, Sb: —0.31% to 0.0%, Al: —0.09% to 0.0%, Te: —0.48% to 0.0%, Al: —0.34% to + 0.36%, Se: 0.0% to + 0.25%, Al: —0.55% to + 0.43%, Mo: —0.13% to 0.0%, Al: 0.0% to + 0.39%, Hg: 0.0% to +0.38%, Al: —0.46% to 0.0%, Au: 0.0%, Al: —0.71% to + 0.27%, Pt: 0.0% to + 0.34%, Al: 0.0% to + 0.37%, Re: 0.0% to + 0.40%, Al: 0.0% to + 0.48%.

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30–38 mg of arsenic, 47–58 mg of antimony, 44–68 mg of tellurium, 59–60 mg of selenium, 32–39 mg of molybdenum, 68–85 mg of mercury, 9–23 mg of gold, 23–28 mg of platinum or 31–38 mg of rhenium were separated from 61–76 mg of uranium.

The metals were recovered with an accuracy of:

As: —0.25% to + 0.15%, U: 0.0% to + 0.44%, Sb: 0.0% to + 0.47%, U: —0.22% to + 0.0%, Te: 0.0%, U: —0.08% to + 0.26%, Se: 0.0% to + 0.18%, U: 0.0% to + 0.55%, Mo: —1.1% to 0.0%, U: 0.0% to + 1.6%, Hg: 0.0% to + 0.4%, U: 0.0% to + 0.89%, Au: 0.0%, U: 0.0% to + 0.33%, Pt: —0.21% to 0.0%, U: 0.0% to + 0.33%, Re: 0.0% to + 0.4%, U: 0.0% to + 0.22%.

Notes

1. Even A.R. caustic soda contains aluminium as an impurity; errors can be compensated by adding an equal volume of caustic soda solution before standardizing the solution of aluminium or uranium.
2. As molybdenum also gives a precipitate with oxine, even a trace of it passing into the filtrate gives high results.

SUMMARY

2 *N* Sodium sulphide can be used to separate arsenic, antimony, tellurium, selenium, molybdenum, mercury, gold, platinum or rhenium from aluminium or uranium.

RÉSUMÉ

Les auteurs proposent l'emploi du sulfure de sodium 2 *N* comme réactif pour la séparation de l'arsenic, de l'antimoine, du tellure, du sélénium, du molybdène, du mercure, de l'or, du platine ou du rhénium d'avec l'aluminium ou l'uranium.

ZUSAMMENFASSUNG

Mit Hilfe von 2 *N* Natriumsulfidlösung kann eine Trennung von Arsen, Antimon, Tellur, Selen, Molybdän, Quecksilber, Gold, Platin oder Rhenium vom Aluminium oder Uran erzielt werden.

REFERENCES

[1] I. K. Taimni and R. P. Agarwal, *Anal. Chim. Acta*, 9 (1953) 121.
[2] I. K. Taimni and R. P. Agarwal, *Anal. Chim. Acta*, 10 (1954) 312.
[3] G. B. S. Salaria, *Anal. Chim. Acta*, 17 (1957) 395.
[4] I. K. Taimni and R. P. Agarwal, *Anal. Chim. Acta*, 9 (1953) 203.
[5] I. K. Taimni and G. B. S. Salaria, *Anal. Chim. Acta*, 12 (1955) 519.
[6] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffmann, *Applied Inorganic Analysis*, John Wiley and Sons, New York 1953, p. 507.
[7] Arthur I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 1953, p. 471.

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SOME QUANTITATIVE REMARKS ON EXTRACTION EQUILIBRIA. III

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In previous papers[1,2], equations which describe the extraction of metal chelates were derived and their validity was proved. In this final part, the use of these equations in analytical chemistry is described. It is therefore necessary to know a number of constants which hitherto have been seldom required.

Some of these constants can easily be determined, *e.g.* the solubility of a metal chelate in an organic solvent. The results of several determinations are shown in Table I.

TABLE I

Chelate	*Solubility in mmoles/ml*
$CuOx_2$	$3.4 \cdot 10^{-3}$
$NiOx_2$ (2 b.a.)	$5.0 \cdot 10^{-2}$
$UO_2Ox_2 \cdot HOx$	$2.8 \cdot 10^{-3}$
$AlOx_3$	$3.8 \cdot 10^{-2}$
$FeOx_3$	$1.5 \cdot 10^{-2}$
$ThOx_4$	$3.4 \cdot 10^{-3}$

Other constants can easily be determined from the given extraction formulae. From the formula

$$\frac{m^{+n}\,\text{res.}}{a} = \frac{fL_{\mathrm{MR}_n}}{(\mathrm{R}^-)^n\mathrm{MR}_n\text{sat.} + fL_{\mathrm{MR}_n}}$$

L_{MR_n} can be calculated, if the percentage of extraction (giving m^{+n} res./a) is determined under known conditions (f and R^- known) and if MR_n sat. is known.

Example: To 1 mg of uranyl ion in 50 ml of aqueous solution a few drops of sulphuric acid were added, and the solution was shaken for 10 min with a solution of 100 mg of oxine in 10 ml of chloroform. After separation of the layers, the pH of the aqueous solution and the uranyl content of the chloroform phase were determined.

From the values obtained the values of $L_{\mathrm{UO_2Ox_2}}$ are calculated (Table II).

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TABLE II

pH	*mg UO_2^{+2} extracted*	$\frac{m^{+2}\ res.}{a}$	$L_{UO_2Ox_2}$ *calc.*
2.80	0.05	0.95	$2.54 \cdot 10^{-25}$
2.86	0.09	0.91	$2.22 \cdot 10^{-25}$
2.99	0.19	0.81	$2.88 \cdot 10^{-25}$
3.13	0.39	0.61	$3.44 \cdot 10^{-25}$
3.18	0.52	0.48	$2.96 \cdot 10^{-25}$
3.47	0.87	0.13	$3.30 \cdot 10^{-25}$
3.55	0.94	0.06	$2.68 \cdot 10^{-25}$
3.90	1.00	0.00	—
		mean value	$2.9 \cdot 10^{-25}$

The reasonable constancy of the solubility product is another proof of the correctness of our considerations. The values found in this way are given in Table III where the previous known values are also shown.

TABLE III

Chelate	*Solubility product*
$CuOx_2$	$5 \cdot 10^{-29}$
$NiOx_2$ (2 b.a.)	$7 \cdot 10^{-23}$
UO_2Ox_2 (HOx)	$2.9 \cdot 10^{-25}$
$AlOx_3$	$1.2 \cdot 10^{-35}$
$FeOx_3$	$7.5 \cdot 10^{-45}$
$ThOx_4$	$6.2 \cdot 10^{-47}$

The complete calculations have been described[3].

THE PREDICTION OF THE CONDITIONS FOR A SEPARATION BY EXTRACTION

If all the necessary constants are known, the conditions for a possible separation can be calculated; or it can be shown that a separation of two elements is impossible under all conditions, with a particular reagent and a particular solvent. Some examples of each case are given below.

1. *The separation of copper and uranyl with oxine–chloroform*

Only conditions in which $f = 5$ are considered; it will be seen later that variation of f within practical limits has little effect.

For a proper separation at least 98% of one of the elements must be extracted while not more than 2% of the other element should be extracted. It is therefore necessary to know the pH required and the amount of oxine which should be present so that more than 98% of the copper can be extracted with 10 ml of chloroform without more than 2% of the uranyl ion being extracted.

Substituting the requirement, Cu^{+2} res.$/a \leqslant 0.02$ and the known values, $f = 5$, $L_{CuOx_2} = 5 \cdot 10^{-29}$, and $CuOx_2$ sat. $= 3.4 \cdot 10^{-3}$, in the extraction formula :

$$\frac{Cu^{+2}\text{ res.}}{a} = \frac{f\,L_{CuOx_2}}{CuOx_2\text{ sat. }(Ox^-)^2 + f\,L_{CuOx_2}}$$

gives $(Ox^-)^2 \geqslant 3.6 \cdot 10^{-24}$.
Substituting the requirement, $UO_2{}^{+2}$ res./$a \geqslant 0.98$ and the known values, $f = 5$, $L_{UO_2Ox_2} = 2.9 \cdot 10^{-25}$, and UO_2Ox_2 sat. $= 2.8 \cdot 10^{-3}$, in the extraction formula gives $(Ox^-)^2 \leqslant 1.1 \cdot 10^{-23}$.

Combination of these results shows that for the separation of copper and uranyl:

$$3.6 \cdot 10^{-24} \leqslant (Ox^-)^2 \leqslant 1.1 \cdot 10^{-23} \quad \ldots\ldots\ldots\ldots \quad (1)$$

By means of table I, given in part II of this series[2], this requirement can be translated into actual conditions of pH and amount of oxine.

Suppose that we want to use 100 mg of oxine, or

$$B = \frac{100}{145} \cdot \frac{1}{50} = 1.38 \cdot 10^{-2} \text{ and } B^2 = 1.90 \cdot 10^{-4}.$$

When all terms in (1) are divided by $B^2 = 1.90 \cdot 10^{-4}$, then:

$$1.9 \cdot 10^{-20} \leqslant (Ox^-)^2_{B=1} \leqslant 5.8 \cdot 10^{-20}$$

and this can directly be "translated" into pH values by means of the above table I. By linear interpolation, it is found that the separation is possible between pH 2.57 and 2.71.

This result was checked by placing known amounts of copper and uranyl ions in 50 ml of a buffer solution of pH 2.60[4] and extracting this solution once with 100 mg of oxine in 10 ml of chloroform. The copper content of the chloroform extract was determined by measuring the absorbance at 450 mμ and the pH of the aqueous phase was measured.

The pH of the aqueous phase was then brought to a value of 5 ± 0.5 with 2 *N* sodium hydroxide and uranyl oxinate was extracted with 10 ml of chloroform. In this extract the uranyl content was found by measuring the absorbance at 530 mμ*.

Because of the relatively large amount of oxine that remains in the aqueous phase after the first extraction, the uranyl oxinate can be extracted without further addition of oxine. This can easily be calculated. At pH 2.60, $\bar{R}_{B=1} = 1.5 \cdot 10^{-10}$, hence in these extractions ($B = 1.38 \cdot 10^{-2}$) $R^- = 2.1 \cdot 10^{-12}$. With K^a_{HR}, it can thus be calculated that $HR_w = 4.0 \cdot 10^{-5}$. From this value we calculate, using K^b_{HR} that $H_2R^+ = 1.2 \cdot 10^{-2}$, and using E_{HR} that $HR_o = 8.2 \cdot 10^{-3}$. Finally $V_w = 50$ and $V_o = 10$ are known, hence $Ox^-_w = 1.0 \cdot 10^{-10}$ mmoles, $HOx_w = 2.0 \cdot 10^{-3}$ mmoles, $H_2Ox^+_w = 6.0 \cdot 10^{-1}$ mmoles, $HOx_o = 8.2 \cdot 10^{-2}$ mmoles. Of the starting quantity of oxine, $6.9 \cdot 10^{-1}$ mmoles, there remains $6.0 \cdot 10^{-1}$ mmoles in the aqueous phase after the first extraction. In this calculation the small quantity of oxine (3.10^{-2} mmoles) extracted as copper oxinate is neglected.

The results of three checks are shown in Table IV.

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* Although measuring the absorbance at 530 mμ is less sensitive than at 450 mμ, the former wavelength was chosen because of the better selectivity.

TABLE IV

mg added		pH aqueous phase	mg found	
copper	*uranyl*		*copper*	*uranyl*
1.00	1.00	2.60	0.98	1.00
0.20	1.00	2.60	0.20	1.00
1.00	0.20	2.62	0.99	0.21

2. *The separation of iron and uranyl*

In the same way, it can be calculated that the separation of iron and uranyl must be possible between pH values of 1.76 and 2.71 with 100 mg of oxine; iron oxinate is then extracted, while uranyl ion is extracted after the pH has been brought to 5 ± 0.5.

The results of two separations carried out under these conditions are shown in Table V.

TABLE V

mg added		pH aqueous phase	mg found	
iron	*uranyl*		*iron*	*uranyl*
0.053	1.06	1.94	0.053	1.06
0.053	1.06	1.97	0.051	1.06

3. *The separation of iron and aluminium*

For the separation of iron and aluminium it is calculated that, with 100 mg of oxine, the pH must lie between 1.76 and 2.70; iron oxinate is then extracted, while aluminium is extracted after the pH has been brought to about 4.5. The results of two separations carried out under these conditions are shown in Table VI.

TABLE VI

mg added		pH aqueous phase	mg found	
iron	*aluminium*		*iron*	*aluminium*
0.053	0.200	1.96	0.053	0.203
0.053	0.200	1.89	0.053	0.200

For rapid and complete extraction of aluminium oxinate with chloroform after iron had been extracted, it proved necessary to allow the solution to stand for half an hour after it had been adjusted to a pH of about 4.5. This had already been observed by CLAASSEN, BASTINGS AND VISSER[5].

4. *The separation of aluminium and uranyl*

By calculations similar to those in the above three examples, the requirements Al^{+3} res./$a \leqslant 0.02$ and UO_2^{+2} res./$a \geqslant 0.98$, lead to the contradiction: $Ox^- \leqslant 3.3 \cdot 10^{-12}$ (uranyl) and $Ox^- \geqslant 2.0 \cdot 10^{-11}$ (aluminium)

If the conditions for the reverse extraction are calculated, *i. e.* at least 98% of the uranyl ion present is to be extracted without extracting more than 2% of the aluminium present, then UO_2^{+2} res./$a \leqslant 0.02$ and Al^{+3} res./$a \geqslant 0.98$, another contradiction is obtained: $Ox^- \geqslant 1.6 \cdot 10^{-10}$ (uranyl) and $Ox^- \leqslant 3.2 \cdot 10^{-12}$ (aluminium).

These contradictions mean that the separation of aluminium and uranyl with oxine and chloroform is impossible under any conditions.

5. *The separation of uranyl and thorium*

In the same way it can be calculated that the separation of uranyl and thorium with oxine and chloroform is also impossible.

THE INFLUENCE OF *f*

It has been shown that some separations are impossible under any conditions. But at the start the restriction was made that only extractions in which $f = 5$ would be considered; thus such separations might be achieved by an extraction in which f had a different value. The influence of the value of f cannot be easily seen from the equations, but it appears when a definite problem is dealt with.

Consider the system water–oxine–chloroform.

In the equation

$$R^- = \frac{K_w K_a f \cdot B}{K_w H^+ (E+f) + f \{K_b (H^+)^2 + K_w K_a\}}$$

the value of each of the three terms of the denominator is calculated from the values $K_w = 10^{-14}$, $K_a = 10^{-10}$, $K_b = 10^{-9}$, $E = 200$; f is negligible with respect to E in the term $(E + f)$.

TABLE VII

pH	H^+	$K_w \cdot H^+(E+f)$	$f \cdot K_b(H^+)^2$	fK_wK_a	*Case*
1	10^{-1}	$2 \cdot 10^{-13}$	$10^{-11} \cdot f$	$10^{-24} \cdot f$	A
4	10^{-4}	$2 \cdot 10^{-16}$	$10^{-17} \cdot f$	$10^{-24} \cdot f$	A — B
7	10^{-7}	$2 \cdot 10^{-19}$	$10^{-23} \cdot f$	$10^{-24} \cdot f$	B
10	10^{-10}	$2 . 10^{-22}$	$10^{-29} \cdot f$	$10^{-24} \cdot f$	B — C
13	10^{-13}	$2 \cdot 10^{-25}$	$10^{-35} \cdot f$	$10^{-24} \cdot f$	C

From a practical point of view the value of f cannot vary to a large extent. For the subdivision into three cases the value $f = 10$ is assumed.

A. For the value of R^-, the second term in the denominator is the deciding one, thus we may write:

$$R^- = \frac{K_w K_a f \cdot B}{K_b (H^+)^2 \cdot f} = \frac{K_w K_a B}{K_b (H^+)^2}$$

and for the extraction error:

$$\frac{m^{+n}\text{ res.}}{a} = \frac{fL}{\left(\dfrac{K_w K_a B}{K_b (H^+)^2}\right)^n MR_n\text{ sat.} + fL}$$

Hence if f increases (less organic solvent) the extraction error increases too.

References p. 510

B. The first term is the deciding one, thus

$$\mathrm{R}^- = \frac{K_a f \cdot B}{\mathrm{H}^+ E}, \text{ and } \frac{m^{+n} \text{ res.}}{a} = \frac{fL}{\left\{\frac{K_a f \cdot B}{\mathrm{H}^+ E}\right\}^n \mathrm{MR}_n \text{ sat.} + fL} = \frac{L}{pf^{n-1} + L},$$

$$\text{in which } p = \left(\frac{K_a \cdot B}{\mathrm{H}^+ E}\right)^n \mathrm{MR}_n \text{ sat., independent of } f.$$

If f increases, the extraction error decreases in all cases except for monovalent metal ions when the extraction error is independent of f.

C. The third term in the denominator is deciding, thus

$$\mathrm{R}^- = \frac{K_w K_a f \cdot B}{K_w K_a \cdot f} = B \text{ and } \frac{m^{+n} \text{ sat.}}{a} = \frac{fL}{B^n \cdot \mathrm{MR}_n \text{ sat.} + fL}, \text{ analogous to A.}$$

As a rule, the influence of f is small, therefore when we deal with extractions to which these considerations apply, only the variations of pH and reagent concentrations need be considered.

SUMMARY

The author shows how the equations derived and proved in the two previous papers can be useful in analytical chemistry. The solubility product of some oxinates is determined. The conditions for separation of Cu/UO_2, Fe/UO_2 and Fe/Al by extraction are calculated and shown to be correct. The separation of Al/UO_2 and UO_2/Th by extraction with oxine-chloroform are proved impossible under any conditions.

RÉSUMÉ

L'auteur montre l'utilité en chimie analytique des équations proposées dans les deux premiers articles de cette série. Les produits de solubilité de quelques oxinates ont pu être déterminés ainsi que les conditions de séparation par extraction des mélanges Cu/UO_2, Fe/UO_2 et Fe/Al.

ZUSAMMENFASSUNG

Es wird gezeigt, dass die in den beiden früheren Veröffentlichungen erwähnten Gleichungen sich mit Vorteil in der analytischen Chemie verwenden lassen; so konnte mit deren Hilfe das Löslichkeitsprodukt einiger Oxinate bestimmt und die Bedingungen für eine Trennung von Cu/UO_2, Fe/UO_2 und Fe/Al durch Extraktion errechnet werden.

REFERENCES

[1] M. OOSTING, *Anal. Chim. Acta*, 21 (1959) 301.
[2] M. OOSTING, *Anal. Chim. Acta*, 21 (1959) 397.
[3] M. OOSTING, *Thesis*, Delft 1958.
[4] W. M. CLARK, *The determination of hydrogen ions*, Williams & Wilkins, Baltimore 1928.
[5] A. CLAASSEN, L. BASTINGS AND J. VISSER, *Anal. Chim. Acta*, 10 (1954) 373.

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SEPARATION AND DETERMINATION OF TITANIUM IN STAINLESS STEELS

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Numerous sensitive organic reagents are known for the spectrophotometric determination of titanium but WELLER's[1] hydrogen peroxide method is still widely used in the analysis of stainless steels owing to its selectivity. Even this reaction cannot be applied directly in presence of coloured cations, *e.g.* Fe^{+3}, Cr^{+3}, Ni^{+2} etc., or in presence of Mo, V, etc., which form colours. Some procedures have been reported where the interferences are compensated[2-4] either in the blank or in the standards. Other procedures involve the chemical separation of some of the interfering ions and compensation for the rest, but none of these is quite satisfactory. Alternatively, titanium is separated chemically[5,6] before its colorimetric determination. The procedure recommended in this paper consists of coprecipitation of titanium along with zirconium as the phosphate after separation of iron by extraction with ether, conversion of the phosphates to sulphates, and spectrophotometric determination with hydrogen peroxide.

EXPERIMENTAL

Titanium sulphate solution. "M & B" titania was fused with potassium bisulphate and dissolved in 5% (v/v) sulphuric acid. The solution was standardized by the peroxide method against a solution of spec-pure titania as sulphate. 1 ml contained 0.66 mg Ti.

Zirconyl chloride solution. B.D.H. Zirconyl chloride was dissolved in hydrochloric acid, precipitated with ammonium hydroxide, and redissolved in a slight excess of hydrochloric acid. The zirconia content of the solution was determined by precipitation with ammonium hydroxide and ignition to ZrO_2; 20 ml contained 60.0 mg Zr. This solution did not contain titanium.

Other reagents. B.D.H. AnalaR or E. Merck reagent quality.

All absorption measurements were made on a Beckman spectrophotometer Model DU with 1.00-cm corex cells.

Estimation of titanium in stainless steels was often required in this laboratory. Attempts to extend the tannin method[7] were without success. Further experiments to separate titanium by precipitation as phosphate were also unsuccessful but the results obtained are worth summarizing here. Titanium is quantitatively precipitated as the phosphate above pH 0.7. At pH 0.7, molybdenum, tungsten and vanadium are quantitatively separated from titanium by a single precipitation. But iron and chromium are strongly coprecipitated and are not removed completely by washing. Hence, coprecipitation of titanium along with zirconium at still higher acidity was resorted to.

Quantitative coprecipitation of titanium

To determine the minimum quantity of zirconium required for quantitative coprecipitation of titanium, varying quantities of zirconium and titanium solutions were mixed and the acidity was adjusted to 2 to 4 *N* with hydrochloric or sulphuric acids in a total volume of 150 ml. The solution was warmed to about 50°, and titanium and zirconium were precipitated with 20 g of diammonium hydrogen phosphate. The precipitate was allowed to settle for 5 to 10 min, filtered through Whatman No. 541 filter paper, and washed four or five times with wash liquid (10 g of the phosphate and 10 ml of conc. hydrochloric acid per l). With more acid in the wash liquid, coprecipitated titanium phosphate was found to dissolve slowly. The phosphates dissolved on heating with oxalic acid, but on addition of acid for the colorimetry of titanium with peroxide, slow precipitation was observed which could not be prevented by increasing the oxalic acid concentration. Hence the phosphate precipitate was transferred back to the original beaker with a jet of hot water, and the solution was made alkaline with sodium hydroxide, boiled for 3–5 min, filtered through the same paper and washed with 2% sodium hydroxide solution. The precipitate was dissolved in 10 ml of 1:1 sulphuric acid, 1 ml of 30 vol. hydrogen peroxide was added and it was then filtered through the same paper. The filtrate was made up to 100 ml and the titanium content was estimated using a spectrophotometer.

The results (Table I) show that 1.32 mg titanium required a minimum of 60 mg of zirconium for quantitative coprecipitation at an acidity of 2–4 *N*.

TABLE I

RECOVERY OF TITANIUM BY COPRECIPITATION ALONG WITH ZIRCONIUM UNDER DIFFERENT CONDITIONS

Titanium solution taken mg of Ti	*Zirconyl chloride added mg of Zr*	*Acidity of precipitation N*	*Titanium recovered mg*	*Difference mg*
0.33	15	2	0.25	−0.08
0.33	30	2	0.32	−0.01
0.33	45	2	0.33	0.0
0.33	60	2	0.33	0.0
0.33	30	4	0.32	−0.01
0.33	45	4	0.32	−0.01
0.33	60	4	0.33	0.0
2.31	60	2	2.29	−0.02
2.31	75	2	2.30	−0.01
2.31	75	3	2.01	−0.30
2.31[a]	80	3	2.03	−0.28
1.32	60	3	1.32	0.00
1.32	60	4	1.31	−0.01

[a] 25 g phosphate used for precipitation.

SEPARATION OF IRON, CHROMIUM AND NICKEL

Titanium was determined using the above procedure in synthetic mixtures with iron, chromium and nickel (Table II). Chromium and nickel do not interfere whereas iron is partly coprecipitated. Hence iron was previously removed by ether extraction[8] from 6 *N* hydrochloric acid solution (Expts. 7–10). The presence of chromium and nickel gave no difficulty.

TABLE II

SEPARATION OF TITANIUM FROM IRON, CHROMIUM AND NICKEL

No.	*Titanium solution taken mg of Ti*	*Ferric chloride taken mg of Fe*	*Chromium chloride taken mg of Cr*	*Nickel chloride taken mg of Ni*	*Titanium found mg*	*Difference mg*
1	0.66	100	—	—	0.77	+ 0.11
2	0.66	100	—	—	0.76	+ 0.10
3	0.66	—	30	—	0.66	0.00
4	0.66	—	30	—	0.67	+ 0.01
5	0.66	—	—	10	0.66	0.00
6	0.66	—	—	10	0.67	+ 0.01
7	0.66	100	30	10	0.66	0.00
8	0.66	100	30	10	0.65	— 0.01
9	0.33	100	30	10	0.33	0.00
10	0.20	100	30	10	0.21	+ 0.01

To study the possible interference of niobium and tantalum, oxalate solutions of niobium and tantalum were added to a standard steel sample solution. Spectrophotometric determination of titanium was carried out in the presence of 0.2 g of oxalic acid. The results are given in Table III along with synthetic and stainless steel samples.

TABLE III

ANALYSIS OF SAMPLES OF STEEL FOR TITANIUM

No.	*Approximate composition of synthetic mixtures %*										*Titanium found %*	*Difference %*
	Fe	*Cr*	*Ni*	*V*	*Mo*	*Mn*	*Al*	*Cu*	*W*	*Ti*		
1	64.0	18.0	8.0	2.0	1.0	0.8	3.0	1.0	2.0	0.071	0.07	+ 0.001
2	56.0	25.0	10.0	—	—	0.8	4.0	2.0	2.0	0.17	0.17	0.0
3	73.0	10.0	10.0	3.5	—	0.8	—	—	2.0	0.43	0.44	+ 0.01
4	82.0	10.0	2.0	—	5.0	0.8	—	—	—	0.53	0.51	— 0.02
5	69.0	5.0	5.0	2.0	2.0	5.0	5.0	5.0	2.0	0.33	0.32	— 0.01
6	48.0	10.0	—	—	—	30.0	5.0	5.0	2.0	0.66	0.65	— 0.01
7	Samples of standard steel supplied by British Chemical Standards (No. 235, 18/8 stainless steel)									0.62	0.62	0.0
8	Samples of standard steel supplied by British Chemical Standards (No. 235, 18/8 stainless steel)									0.62	0.61	— 0.01
9	Same B.C.S. Sample (0.1 g) + 2 mg Cb + 2 mg Ta added									0.62	0.61	— 0.01
10	Same B.C.S. Sample (0.1 g) + 2 mg Cb + 2 mg Ta added									0.62	0.60	— 0.02

PROCEDURE

Stainless steel samples were analyzed by the following procedure: dissolve 0.1 g of a homogeneous sample in 20 ml of 1:1 hydrochloric acid by warming, add about 1 ml of nitric acid and boil. Cool, neutralize with ammonium hydroxide and then add conc. hydrochloric acid to bring the acidity to 6 *N*. Cool to room temperature, transfer to a separating funnel and extract three times with 50-ml aliquots of ether.

Take the aqueous layer into a 400-ml beaker, heat to expel the ether, add 20 ml of zirconyl chloride solution, dilute to twice the volume and precipitate with 20 g diammonium hydrogen phosphate. Allow to settle for 5 to 10 min, filter through Whatman No. 541 filter paper, wash four or five times with the wash liquid and transfer the precipitate back to the original beaker with a jet of hot water. Make the solution alkaline with sodium hydroxide, boil for 1 min filter through the same paper and wash with 2% sodium hydroxide solution. Transfer the precipitate back to the original beaker with a jet of hot water, dissolve in 10 ml of 1:1 sulphuric acid, add 1 ml of 30 volumes hydrogen peroxide and 0.2 g oxalic acid, dilute to about 50 to 75 ml and filter through the same paper. Dilute the filtrate and washings to 100 ml. Measure the optical density of the solution and compute the titanium content from a calibration curve obtained under similar conditions (it is important to add the same amount of oxalic acid).

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SUMMARY

Titanium is separated from titanium-bearing stainless steels by coprecipitation with zirconium as phosphate from 2–3 *N* acid solutions after removal of iron by ether extraction. It is spectrophotometrically determined by the hydrogen peroxide method in the presence of oxalic acid, with an accuracy better than ± 0.02%. V, Fe, Cr, Ni, Al, Cu, Mo, W, Nb, and Ta do not interfere.

RÉSUMÉ

Lors de l'analyse des aciers inoxydables, le titane peut être séparé par coprécipitation avec le zirconium au moyen de phosphate, après extraction du fer par l'éther. Il est finalement dosé spectrophotométriquement par la méthode au peroxyde d'hydrogène en présence d'acide oxalique.

ZUSAMMENFASSUNG

Zur Bestimmung von Titan in titanhaltigen Edelstählen wird zunächst das Eisen nach dem Aether-Extraktionsverfahren entfernt; Titan wird dann zusammen mit Zirkon als Phosphate gefällt und ersteres nach der Wasserstoffperoxyd-Methode spektrophotometrisch bestimmt.

REFERENCES

[1] A. WELLER, *Ber.*, 15 (1882) 2593.

[2] F. W. HAYWOOD AND A. A. R. WOOD, *Metallurgical analysis by means of Spekker photoelectric absorptiometer*, Adam Hilger, Ltd. London 1957, p. 212.

[3] HIDEHIRO GOTO, YACHIYO KAKITA AND KICHINOSUKE HIRA KAWA, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 78 (1957) 1337.

[4] L. SOMMER, *Collection Czechoslov. Chem. Communs.*, 22 (1957) 1793.

[5] W. F. PICKERING, *Anal. Chim. Acta*, 12 (1955) 572.

[6] J. R. SIMMLER, K. H. ROBERTS AND S. M. TUTHILL, *Anal. Chem.*, 26 (1954) 1902.

[7] M. SANKAR DAS, CH. VENKATESWARLU AND V. T. ATHAVALE, *Analyst*, 81 (1956) 239.

[8] E. B. SANDELL, *Colorimetric determination of traces of metals*, Interscience Publishers, New York 1950, p. 34.

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MICRO-HETEROMETRIC DETERMINATION OF BISMUTH BY TITRATION WITH THIOCARBANILIDE

A STUDY OF THE REACTION AND THE COMPOUNDS

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INTRODUCTION

Complex compounds of bismuth and thiourea have been reported by several investigators. Yellow or orange coloured solutions are obtained which can be used for the photometric determination of bismuth. The structure of these complexes is not known; different workers have suggested that the complexes contain a definite number of molecules of thiourea per atom of bismuth, this number varying from two to six[1].

We were interested in studying the heterometric behaviour of derivatives of thiourea-bismuth complex cations with large anions. We used the iodobismuthate anion, the properties of which had already been studied[2]. Fairly large salt complexes of strictly stoichiometric composition were obtained and used for the heterometric determination of minute quantities of bismuth. Thus, *ca.* 0.2 mg of bismuth in 20 ml of a solution containing sufficient thiocarbanilide (TCA) could be precisely determined by titration with potassium iodide. The titration at room temperature usually took 7–15 min, and the error was negligible. The analyzed solution could contain *ca.* 99% of many metals, including thorium and uranium(VI). Part of the work deals with the study of the different compounds obtained.

EXPERIMENTAL

The apparatus and working conditions were the same as in previous heterometric investigations[3].

All chemicals used were either AnalaR or chemically pure reagents. Special solutions were prepared as follows:

Bismuth nitrate, M. 48.5 g. of Bi $(NO_3)_3 \cdot 5H_2O$ (Baker's Analyzed), were dissolved in 20 ml of conc. nitric acid and diluted to 100 ml. A 0.1 *M* solution in 2 *M* nitric acid was then prepared. More dilute solutions were prepared from this solution by dilution; the 0.0005 *M* solution was 0.1 *M* in nitric acid.

Thiocarbanilide, 0.01 *M.* 0.5707 of TCA (Eastman Organic Chemicals, Cat. No. 245), was dissolved in *ca.* 95% alcohol and diluted to 250 ml. More dilute 50% alcoholic solutions of TCA were prepared from this standard solution.

Potassium iodide, 0.1 *M,* aqueous. (Baker's Analyzed).

RESULTS AND DISCUSSION

When bismuth nitrate and thiocarbanilide solutions were mixed, no visible change occurred, but when potassium iodide was added, an orange precipitate appeared. As TCA seemed insoluble in water, a 50% alcoholic solution was used. Only a little TCA could be added to the analyzed solution without precipitation. If the solution contained too little alcohol, the TCA precipitated, which ruined the heterometric titration. But the insoluble Bi–TCA–I$^-$ compound obtained dissolved in excess of alcohol. In spite of these difficulties, conditions were found for the study of the insoluble compounds obtained, and for the determination of bismuth.

Titrations of bismuth with TCA

The results of such titrations are given in Table I. Bismuth could be titrated with TCA only if the analyzed solution contained bismuth and iodide in a ratio of $1:\geq 8$ (Expts. 1–7). If less iodide was present, then only that part of the bismuth corresponding to the ratio of $1[\mathrm{Bi}]:8[\mathrm{I}^-]$ was titrated (Expts. 8–13). Two moles of TCA were always consumed at the first maximum density point per one mole of *titrated* bismuth. Any iodide present in excess of the above ratio had no influence. The use of a red filter did not improve the results, the maximum optical density value achieved being sometimes even lower with a filter than without. The compound obtained at the first maximum density point always had the stoichiometric composition $\mathrm{Bi_1(TCA)_2I_8}\downarrow\downarrow$ (or $\mathrm{Bi_1H_m(TCA)_2I_8}$). The smallest amount of bismuth which could easily be titrated was *ca.* 0.2 mg of bismuth (in 20 ml solution).

Titrations of TCA with bismuth nitrate

Some of the experiments carried out are presented in Table II and Fig. 1. When 5 ml of 0.0025 *M* (*ca.* 3.0 mg TCA) in 20 ml of solution were titrated with bismuth nitrate, the maximum optical density values obtained were rather high (Expts. 1–5) and the results were practically the same whether the $[\mathrm{Bi}]:[\mathrm{I}^-]$ ratio at the end-point was 1:16.7 or 1:4.1. In all these experiments the ratio of [Bi]:[TCA] at the end-point was always 1:4, and the whole TCA present in solution was determined. The amount of potassium iodide in the analyzed solution was gradually diminished in these experiments, but in all cases the molar ratio of $[\mathrm{I}^-]:[\mathrm{TCA}]$ was either 1:1 or higher. However, when less than the above ratio of iodide was present, only that part of TCA corresponding to the ratio of $1[\mathrm{I}^-]:1[\mathrm{TCA}]$ was titrated (Expts. 6–7).

When the titration curves were analyzed, it was found that in almost all cases an intermediate intersection point ($=\downarrow$) was obtained in addition to the final critical point ($=\downarrow\downarrow$). This point always occurred at the molar ratio of $1[\mathrm{Bi}]:8[\mathrm{I}^-]$ (Table II). Again, excess of potassium iodide had no influence.

From the above calculations it may be concluded that the insoluble compound obtained at the end-point had the composition $\mathrm{Bi_1(TCA)_4I_4}\downarrow\downarrow$.

As to the analytical aspect of these titrations, this compound, which has a different composition from that obtained with TCA as titrant, is no longer suitable for the determination of the components. Although the compound $\mathrm{Bi[TCA]_4I_4}$ was obtained stoichiometrically from the components, if the analyzed solution contained potassium iodide in a molar ratio of $[\mathrm{I}^-]:[\mathrm{TCA}] = \geq 1:1$, not less than *ca.* 3 mg of TCA was necessary for the titration of TCA with bismuth. This is more than ten times that needed for the reverse titration (compare Tables I and III).

TABLE I

General composition: 4 ml *mM* $Bi(NO_3)_3$ + 1 ml *M* HNO_3 + *a* ml *nM* KI + (15—*a*) ml H_2O + *x* ml *pM* thiocarbanilide (50% alc) (= TCA) T = 20°

Expt. No.	*$Bi(NO_3)_3$ Molarity*	*KI*		*Titrant Thiocarbanilide (= TCA)*				*Titration time in min*	*Molar ratios at the end-point*		*Remarks*
		Molarity	*ml*	*Molarity*	*Init. ppt. at ml*	*End-point at ml*	*Maximum density value*		*[Bi] : [TCA]*	*[Bi] : [I−]*	
1	0.00025	0.05	5	0.00125	0.4	i 1.6 h	0.395	11	1:2	1:250	
2	0.00025	0.05	1	0.00125	0.4	i 1.60 h	0.328	7	1:2	1:50	
3	0.0005	0.05	2	0.00125	0.2	i 3.2 h	0.638	8	1:2	1:50	
4	0.0005	0.005	5	0.00125	0.4	i 3.18 h	0.429	10	1:2	1:12.5	
5	0.001	0.005	10	0.0025	0.4	i 3.18 sh/h	0.862	11	1:2	1:12.5	Red filter (Corning 3480)
6	0.001	0.005	6.4	0.0025	0.4	i 3.20 h	0.497	11	1:2	1:8	
7	0.001	0.005	6.4	0.0025	0.2	i 3.20 h	0.507	10	1:2	1:8	Red filter
8	0.001	0.005	5	0.0025	0.6	∼ 2.4	0.593	11	1:1.5	1:6	Corresponds to: 3.20 × $^3/_4$ = 2.40 ml TCA
9	0.001	0.005	5	0.0025	0.6	i 2.4 h	0.502	10	1:1.5	1:6	Corresponds to: 3.20 × $^3/_4$ = 2.40 ml TCA red filter
10	0.001	0.005	4	0.0025	0.6	i 2.1 h	0.323	11	1:1.3	1:5	Corresponds to: 3.20 × $^5/_8$ = 2.0 ml TCA
11	0.001	0.005	4	0.0025	0.6	c 2.1 h	0.308	10	1:1.3	1:5	Corresponds to: 3.20 × $^5/_8$ = 2.0 ml TCA red filter
12	0.002	0.005	6.4	0.0025	0.1	c 3.2 h	0.561	10	1:1	1:4	Corresponds to: 4 ml Bi 0.001 *M* at 1[Bi]:8[I^-] = 3.20 ml TCA
13	0.002	0.005	4	0.0025	0.1	i 2.00 h	0.348	7	1:0.625	1:2.5	Corresponds to: 2.5 ml Bi 0.001 *M* at 1[Bi]:8[I^-] = 2.00 ml TCA

i = intersection point; h = horizontal maximum density line; sh = short; c = contact point.

TABLE II

General composition: 5 ml 0.0025 *M* thiocarbanilide (= TCA) + 1 ml *M* HNO_3 + *b* ml 0.005 *M* KI + ad 20 ml H_2O + *x* ml 0.001 *M* $Bi(NO_3)_3$
T = 20°

Expt. No.	*ml KI*	*[I−] : [TCA]*	*Titrant $Bi(NO_3)_2$*				*Titration time in min*	*Calculated molar ratios at the end-point*		*[Bi] : [I−] at the intermediate point*	*Remarks*
			Initial ppt. at ml	*Intermediate point at ml*	*End-point at ml*	*Maximum density value*		*[Bi] : [TCA]*	*[Bi] : [I−]*		
1	10	4:1	0.1	2.5	i 3.00 h	0.92	6	1:4.2	1:16.7	1:20	
2	5	2:1	0.1	2.6	i 3.10 h	0.97	5	1:4	1:8.1	1:9.6	
3	3.3	1.32:1	0.1	2	i 3.10 h	0.74	4	1:4	1:5.3	1:8.2	
4	3	1.2:1	0.1	1.9	i 3.06 h	0.88	5	1:4.1	1:4.9	1:7.9	
5	2.5	1:1	0.1	1.5	i 3.06 h	0.76	5	1:4.1	1:4.1	1:8.3	
6	2	4:5	0.1	—	i 2.44 h	0.69	5	1:5.1	1:4.1		$2.44 \times {}^5/_4 = 3.06$
7	1.5	3:5	0.3	0.95	i 1.9 h	0.49	11	1:6.6	1:4	1:7.9	$1.9 \times {}^5/_3 = 3.1$

= intersection point; h = horizontal maximum density line.

TABLE III

General composition: 4 ml *m*M $Bi(NO_3)_3$ + 1 ml *M* HNO_3 + *a* ml *nM* thiocarbanilide (= TCA) + 1 ml *pM* salt + ad 20 ml H_2O + *x* ml *qM* KI
T = 20°. Content: 0.2 to 0.4 mg bismuth

Expt. No.	*Molarity of $Bi(NO_3)_3$*	*Thiocarbanilide*		*Salt solution*		*Titrant KI*				*Titration time in min*	*% Bismuth*	*[Bi] : [TCA]*	*[Bi]:[I⁻] at the end-point*
		ml	*Molarity*	*Name*	*Molarity*	*Molarity*	*Initial ppt. at ml*	*End-point at ml*	*Maximum density value*				
1	0.0005[a]	2.5	0.002	—	—	0.005	1.0	i 4.00 h	0.57	10		1:2	1:8
2	0.0005	3	0.002	—	—	0.005	1.4	i 3.20 h	0.34	9		1:3	1:8
3	0.0005	4	0.002	—	—	0.005	0.4	i 3.2 h	0.76	6		1:4	1:8
4	0.0005	8	0.002	—	—	0.005	0.4	i 3.20 h	0.86	10		1:8	1:8
5	0.0005	8	0.004	—	—	0.005	0.3	i 3.2	1.01	5		1:16	1:8
6	0.00025	8	0.004	—	—	0.0025	1.4	i 3.23 h	0.43	12		1:32	1:8
7	0.00025	8	0.004	$Ca(NO_3)_2$	1.0	0.0025	0.4	i 3.20 h	0.51	13	0.5	1:32	1:8
8	0.0005	8	0.002	$Ba(NO_3)_2$	0.1	0.005	0.8	i 3.20 h	0.82	13	2.83	1:8	1:8
9	0.0005	8	0.002	$Mg(NO_3)_2$	0.5	0.005	0.8	i 3.2 h	0.78	8		1:8	1:8
10	0.00025	8	0.004	$Mg(NO_3)_2$	1.0	0.0025	0.4	i 3.18 h	0.68	8	0.82	1:32	1:8
11	0.00025	8	0.004	$Zn(NO_3)_2$	0.5	0.0025	0.4	c 3.20 h	0.91	8	0.6	1:32	1:8
12	0.00025	8	0.004	$Zn(NO_3)_2$	1.0	0.0025	1.2	i 3.20 h	0.72	7	0.31	1:32	1:8
13	0.00025	8	0.004	$Ni(NO_3)_2$	0.1	0.0025	1.0	i 3.2	0.61	10	3.2	1:32	1:8
14	0.00025	8	0.004	$Co(NO_3)_2$	0.1	0.0025	0.8	i 3.2 h	0.55	10	3.3	1:32	1:8
15	0.00025	8	0.004	$Al(NO_3)_3$	0.5	0.0025	0.4	i 3.20 h	0.95	8		1:32	1:8
16	0.00025	8	0.004	$Al(NO_3)_3$	0.7	0.0025	1.6	c 3.20 h	0.62	9	1.05	1:32	1:8
17	0.0005	8	0.002	$Cr(NO_3)_3$	0.1	0.005	1.2	i 3.2 h	0.75	16	7.14	1:8	1:8
18	0.0005	8	0.002	$Cd(NO_3)_2$	0.1	0.005	1.4	i 3.21 h	0.64	16	3.4	1:8	1:8
19	0.0005	8	0.002	$Pb(NO_3)_2$	0.1	0.005	0.4	i 3.20 h	0.84	5	1.9	1:8	1:8
20	0.0005	8	0.002	$Th(NO_3)_4$	0.5	0.005	0.6	i 3.20 h	0.91	5	0.34	1:8	1:8
21	0.0005	8	0.002	$UO_2(NO_3)_2$	0.4	0.005	0.2	i 3.20 h	0.82	6	0.42	1:8	1:8
22	0.0005	8	0.002	$ZrO(NO_3)_2$	0.2	0.005	1.2	i 3.2 h	0.62	29	2.15	1:8	1:8
23	0.0005	8	0.002	$Ce(NO_3)_3$	0.125	0.005	0.8	i 3.20 h	0.74	6	2.2	1:8	1:8

[a] 5 ml; i = intersection point; h = horizontal maximum density line; c = contact point.

Titration of bismuth with potassium iodide

Table III and Fig. 2 show the results of titrations of bismuth nitrate with potassium iodide in solutions which contained bismuth and TCA in a ratio between 1:2 and 1:32, and in the presence and absence of foreign metals. In all cases the first maximum density point was at the calculated end-point and the error was negligible. At this point the molar ratio of $[\mathrm{Bi}]:[\mathrm{I}^-]$ was exactly equal to 1:8. This result was independent of the molar ratio of $[\mathrm{Bi}]:[\mathrm{TCA}]$ within the range 1:32 to 1:2. The maximum density values were of course lower at the lowest ratio mentioned above (Expts. 1 and 2). After the end-point a horizontal maximum density line was always obtained. If the maximum density values obtained in Expts. 6, 10, 11 and 12 are compared, it is seen that in the presence of foreign salts the density values achieved were almost twice as high as in the blank experiments. In the case of lead, cadmium, cerium or zirconium, the amount cited in the table was the maximum permissible for a safe titration. In all other cases the amounts cited could be exceeded. Less than 0.3–0.4% of bismuth in uranium or thorium could be determined precisely (Expts.

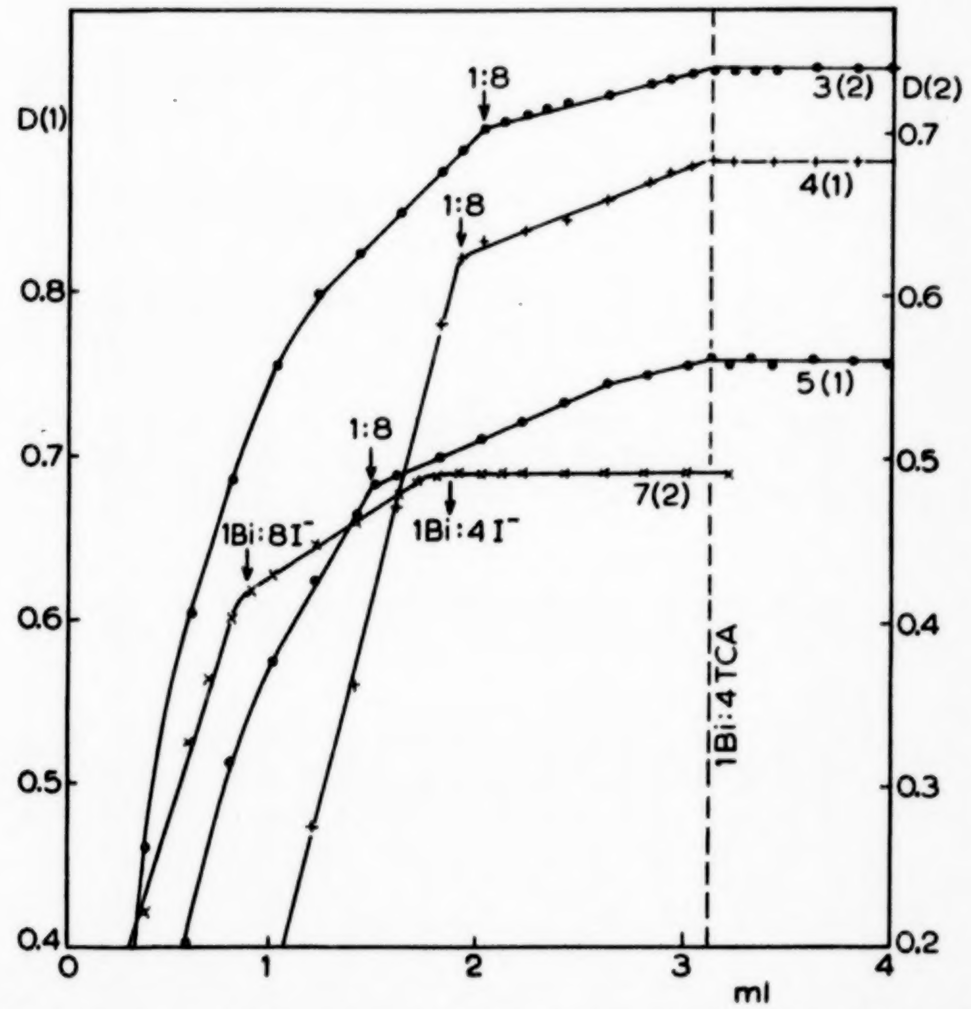

Fig. 1. Titrations of thiocarbanilide–iodide mixtures with bismuth nitrate.

20–21). In the case of magnesium, zinc or aluminium, the bismuth amounted to less than one per cent of the total metal content of the solution. In all other cases (except chromium) the foreign metal amounted to 95% or more. The foreign metal usually acted favourably on the titration.

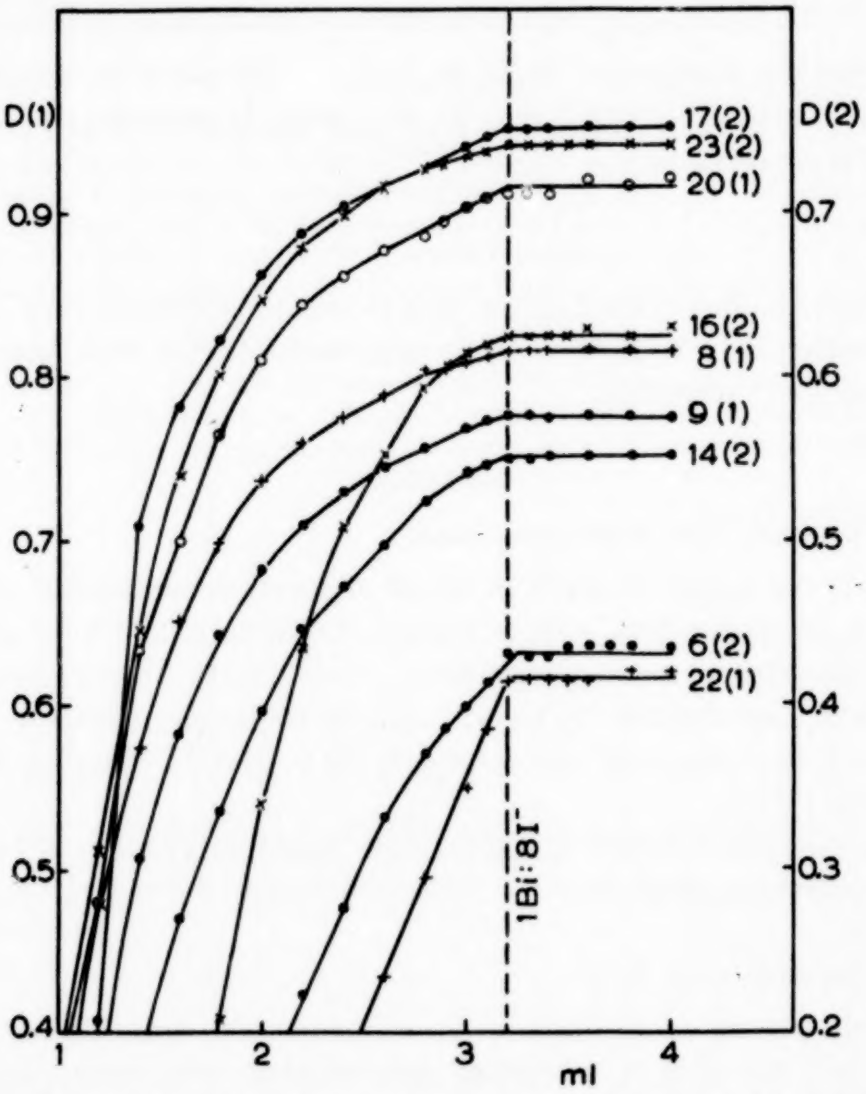

Fig. 2. Titrations of bismuth nitrate–thiocarbanilide mixtures with potassium iodide.

Composition of the compounds

On titrating bismuth with TCA or with potassium iodide, we always found a molar ratio of $[Bi]:[I^-]$ equal to 1:8 in the final compounds obtained. In our previous investigations with bismuth iodide[2], we had never found a compound which contained iodide in excess of this ratio. No reaction between TCA and potassium iodide was traced. Therefore we must conclude that in all the previous cases the iodide entirely complexed the bismuth, and that the complex formed the insoluble compound $(TCA)_2BiI_8\downarrow\downarrow$, or better $(TCA)_2H_mBiI_8\downarrow\downarrow$. Conversely on titrating TCA–iodide mixtures with bismuth nitrate (Table II) we obtained the molar ratio of $1[Bi]:8[I^-]$ at the *intermediate point*. Evidently at this point a compound of the same composition as before was obtained. On further addition of bismuth nitrate, we obtained the final compound $Bi(TCA)_4I_4\downarrow\downarrow$. This compound must be very stable as it was always formed at the final stage. The transformation of $(TCA)_2H_mBiI_8\downarrow$ into $Bi(TCA)_4I_4\downarrow\downarrow$ by further addition of bismuth may be explained differently. Either the latter compound is a neutral insoluble compound in which both the iodide and the TCA are coordinately bound to the bismuth, or a further reaction occurs between the intermediate compound and bismuth nitrate, which might be represented as follows:

$$(TCA)_2BiI_8\downarrow + 6TCA + Bi^{+3} \rightarrow [Bi(TCA)_8]\,[BiI_8]$$

If this were true, the compound $Bi(TCA)_4I_4$ obtained must be doubled and would contain bismuth both as a cation and as an anion. It remains uncertain which of these formulae is correct.

ANALYTICAL ASPECT

Bismuth nitrate can be titrated either with potassium iodide or with TCA (50% alc.). The former titration is to be preferred, the titration of TCA with bismuth as titrant is about ten times less sensitive.

METHODS

1. *Titration of bismuth with potassium iodide*

Approximately 0.2 mg of bismuth in 20 ml of solution containing 1 ml of *M* nitric acid, 1 ml of 0.5 *M* magnesium, zinc or aluminium nitrate, and 8 ml of 0.004 *M* TCA (50% alc.) are titrated at room temperature with 0.0025 *M* potassium iodide. The analyzed solution may contain 95 to 99% of the following metals as cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Cr^{+3}, Cd^{+2}, Pb^{+2}, Th^{+4} ($\gtrless$ 99.7%), U^{+6} ($= UO_2^{+2}$) ($\geqslant$ 99.6%), Zr or Ce^{+3}.

Remark. The end-point comes exactly at the molar ratio 1[Bi]:8[I^-]. The error in this method is always negligible.

2. *Titration of bismuth with TCA*

Approximately 0.5 mg of bismuth in 20 ml of aqueous solution containing 1 ml of *M* nitric and 2–5 ml of 0.05 *M* iodide are titrated with 0.001–0.00125 *M* TCA (50% alc.)

Remark. The end-point is reached exactly at the molar ratio of 1[Bi]:2[TCA].

3. *Titration of TCA with bismuth nitrate*

Approximately 2–2.5 mg of TCA (= 4–5 ml 0.0025 *M*, 50% alc.) in 20 ml of solution, containing 1 ml of *M* nitric acid and *ca.* 1 ml of 0.05 *M* iodide are titrated with 0.001 *M* bismuth nitrate.

Remark. The end-point is reached at the molar ratio of 1[Bi]:4[TCA].

SUMMARY

The composition, structure and behaviour of the large salt complexes formed between thiocarbanilide and bismuth iodide were studied heterometrically. Structural formulae for the compounds are presented. Methods are presented for the exact determination of *ca.* 0.2 mg of bismuth in 20 ml of solution by titration with potassium iodide (or with thiocarbanilide). The analyzed solution could contain 95–99% of the following metals as cations: Ca^{+2}, Ba^{+2}, Mg^{+2}, Zn^{+2}, Ni^{+2}, Co^{+2}, Al^{+3}, Cr^{+3}, Cd^{+2}, Pb^{+2}, Th^{+4}, ($\gtrless$ 99.7%), U^{+6} ($\geqslant$ 99.6%), Zr^{+4} or Ce^{+3}.

RÉSUMÉ

Une étude a été effectuée sur les complexes formés entre iodure de bismuth et thiocarbanilide. Des méthodes de dosage du bismuth sont proposées par titrage hétérométrique au moyen d'iodure de potassium ou de thiocarbanilide.

ZUSAMMENFASSUNG

Die Zusammensetzung, Struktur und das Verhalten des Thiocarbanilid-Wismutjodid Komplexes wurde heterometrisch untersucht. Ferner wird eine titrimetrische Bestimmung von Wismut mit Kaliumjodid oder Thiocarbanilid beschrieben.

REFERENCES

[1] K. A. HOFFMANN AND K. L. GONDER, *Ber.*, 37 (1904) 242; C. MAHR, *Z. anal. Chem.*, 94 (1933) 161; J. V. DUBSKY, A. OKAČ AND B. OKAČ, *Z. anorg. u. allgem. Chem.*, 216 (1934) 386; J. V. DUBSKY, A. OKAČ, A. TRTILEK, *Mikrochemie*, 17 (1935) 332; K. W. GROSSHEIM-KRYSKO, *Z. anal. Chem.*, 121 (1941) 399; O. S. FEDOROVA, *J. Gen. Chem. U.S.S.R.* (Eng. Transl.) 24 (1954) II/59; W. NIELSCH AND G. BÖLTZ, *Z. anal. Chem.*, 142 (1954) 321; N. M. LISICKI AND D. F. BOLTZ, *Anal. Chem.*, 27 (1955) 1722; W. NIELSCH AND G. BÖLTZ, *Metall*, 9 (1955) 856; *C.A.*, 50 (1956) 1517.

[2] M. BOBTELSKY AND M. M. COHEN, *Anal. Chim. Acta*, 20 (1959) 1.

[3] See literature on heterometry, M. BOBTELSKY AND J. EISENSTADTER, *Anal. Chim. Acta*, 20 (1959) 216, 352; M. BOBTELSKY AND J. M. E. GOLDSCHMIDT, *Bull. Research Council Israel*, 7A (1958) 121; M. BOBTELSKY AND J. SHAMIR, *Bull. soc. chim. France*, (1958) 1569.

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THE DETERMINATION OF BORON IN BORIC ACID ESTERS

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INTRODUCTION

The determination of boron in an organic ester of boric acid is usually performed by hydrolysis[1] of the ester and titration of the resulting boric acid in the presence of mannitol[2]. However, with esters of high hydrolytic stability[3] it is necessary to maintain prolonged periods of reflux in boron-free glassware. Often low results are obtained and a second and more prolonged hydrolysis must be performed. In addition, with aromatic or alkanolamine[3,4] esters, the phenols or alkanolamines liberated in the hydrolysis interfere with the titration of the boric acid. Hydrolysis followed by the "identical pH" method[5,6] can be used but has never been reported. In such cases the boron was determined gravimetrically[7,8] or by conversion to methyl borate with sulfuric acid and methanol[9]. This latter procedure adapted from the original method of CHAPIN[10] is at best unwieldy and often suffers from incomplete volatilization of the boron as methyl borate. In addition it is not applicable at all to highly sterically hindered esters such as tri-(2-cyclohexylcyclohexyl)borate and tri-(diisobutylcarbinyl) borate[3] since only a small percentage of these esters are transesterified in a reasonable time.

A general procedure which has been found to be applicable with slight modification to boric acid esters is the method for the determination of boron in acid insoluble minerals[11] which has also been used for the determination of boron in boric acid complexes of hydroxy acids[12,13], hydroxy ketones[13], and catechol[12,14]. The ester is fused with sodium carbonate in a platinum crucible. The cooled melt is dissolved in hydrochloric acid, boiled to expel carbon dioxide, and neutralized with dilute base. Excess mannitol is then added and the boric acid titrated to the phenolphthalein end-point.

EXPERIMENTAL

Reagents and materials

The boric acid esters excluding tri-(1-carboxy-11-heptadecyl) borate have been described.[3] Tri-(1-carboxy-11-heptadecyl) borate was prepared by the azeotropic removal of water (with toluene) from a 3:1 molar mixture of 12-hydroxystearic acid and boric acid. The reaction mixture was then filtered and stripped of toluene under reduced pressure. The residue was triturated with cold acetone and filtered in a dry box to give a 60% yield of white granules melting at 111–120°.

Sodium hydroxide solution was prepared by dissolving reagent grade pellets in an equal weight of distilled water and filtering the insoluble carbonate. The filtrate was diluted to the proper volume and standardized with twice recrystallized boric acid. The recrystallized boric acid was previously dried in a vacuum desiccator over conc. sulfuric acid. All other materials were reagent grade.

The indicator solutions were prepared as follows: Phenolphthalein, 1 g in 100 ml of 60% (by volume) ethanol; methyl red, 0.1 g in 60 ml of methanol; methylene blue, 0.1 g in 100 ml of water.

Carbonate fusion procedure

A 35-ml platinum crucible is lined with sodium carbonate by melting about 4 g of the anhydrous reagent over a Fisher burner and gently swirling the vessel with crucible tongs while cooling. A 0.5 to 1.0 g-sample of the ester is accurately weighed into the crucible and covered (without mixing) with sodium carbonate (23 g) to within $^{1}/_{4}''$ of the crucible top. The crucible is placed in a muffle furnace at room temperature and heated to 850° at which temperature a clear melt is obtained. After cooling, the crucible is placed in a 500-ml wide mouth Erlenmeyer flask and covered with 100 ml of distilled water. Conc. hydrochloric acid (60 ml) is poured down the side of the flask which is then covered with a watch glass. After a few min solution is complete. Methyl red indicator (3 drops) is added and the excess acid neutralized with either a saturated solution of sodium hydroxide (stored in a polyethylene bottle) or sodium hydroxide pellets (8.5 g) and then reacidified with several drops of 4 *N* hydrochloric acid. The slightly acid solution is gently boiled on a hot plate for 10 min and cooled to room temperature in a cold water bath. Three drops of methylene blue solution are added and the solution and cover rinsings are adjusted to the methyl red end-point with 0.1 *N* sodium hydroxide. (The red-violet to green end-point effected by the methylene blue is more accurately discernable than the normal red to yellow change of methyl red itself.) Phenolphthalein (8 drops) and excess mannitol (30 g, the use of less than seven moles of mannitol per mole of boric acid at the dilutions used results in a hazy end-point and low boron determination) are then added and the boric acid complex is titrated with 0.1 *N* sodium hydroxide to the phenolphthalein end-point (green to red-violet).

Modified carbonate fusion procedure

A modified procedure is employed for the alkanolamine borates. A weighed sample is just covered with conc. hydrochloric acid in the platinum crucible and allowed to stand at room temperature overnight. The acid is then neutralized by careful addition of conc. sodium hydroxide solution. Sodium carbonate is added as above and the usual procedure followed.

Blank

A blank determination using the amounts of reagents as specified in the analytical procedure possessed a titer equivalent to 0.11 mg of boron. The percentage boron is thus calculated:

$$\%\ \mathrm{B} = \frac{10.82 \times \mathrm{N} \times \mathrm{ml} - (\text{blank, in mg boron})}{\text{sample wt. (mg)}} \times 100$$

Parr peroxide bomb procedure (adapted from procedure of SNYDER, KUCK AND JOHNSON[15]*)*

The ester sample (0.5 g) is weighed into a PARR bomb fusion cup (Series 2000, 22 ml, electric ignition, macro bomb) followed by one gram of potassium perchlorate and 15 g of sodium peroxide. After thorough mixing with a glass rod, the rod is wiped clean with a small piece of filter paper which is added to the charge and the mixture is ignited with the usual precautions. The fusion mixture is then dissolved in 100 ml

TABLE I

PERCENTAGE BORON IN BORIC ACID ESTERS

Ester	*Formula*	*Calculated*	*Found*		
			Carbonate fusion	*Parr bomb*	*"Identical pH"*
Aromatic:					
Triphenyl borate	$C_{18}H_{15}O_3B$	3.73	3.74		
Tri-*o*-cresyl borate	$C_{21}H_{21}O_3B$	3.26	3.24		
Tri-*o*-chlorophenyl borate	$C_{18}H_{12}O_3Cl_3B$	2.75	2.83	2.84	
Tri-*o*-phenylphenyl borate	$C_{36}H_{27}O_3B$	2.09	2.04		
Tri-*o*-cyclohexylphenyl borate	$C_{36}H_{45}O_3B$	2.02	2.02		
Alkanolamine:					
Triethanolamine borate	$C_6H_{12}O_3NB$	6.89	6.71	6.75	6.73
Triisopropanolamine borate	$C_9H_{18}O_3NB$	5.44	5.47	5.46	
High hydrolytic stability:					
Tri-(diisobutylcarbinyl) borate	$C_{27}H_{57}O_3B$	2.46	2.40	2.36	
Tri-(2-phenylcyclohexyl) borate	$C_{36}H_{45}O_3B$	2.02	2.02		
Tri-(2-cyclohexylcyclohexyl) borate	$C_{36}H_{63}O_3B$	1.95	1.93		
Tri-(2,6,8-trimethyl-4-nonyl) borate	$C_{36}H_{75}O_3B$	1.91	1.92		
Tri-(dicyclohexylcarbinyl) borate	$C_{39}H_{69}O_3B$	1.81	1.79		
Intermediate and low hydrolytic stability:					
Tri-*tert.*-amyl borate	$C_{15}H_{33}O_3B$	3.97	4.08		
Tri-(1,3-dichloro-2-propyl) borate	$C_9H_{15}O_3Cl_6B$	2.74	2.82		
Tri-(*β,β,β,*-trichloro-*tert.*-butyl) borate	$C_{12}H_{18}O_3Cl_9B$	2.00	2.04		
Tri-*n*-dodecyl borate	$C_{36}H_{75}O_3B$	1.91	1.86		
Trioleyl borate	$C_{54}H_{105}O_3B$	1.33	1.35		
Tristearyl borate	$C_{54}H_{111}O_3B$	1.32	1.34		
Tri-(1-carboxy-11-heptadecyl) borate	$C_{54}H_{105}O_9B$	1.19	1.20		

of water in a 400-ml boron-free beaker after which the cup is removed and rinsed. The solution and rinsings are combined and neutralized with conc. hydrochloric acid (approximately 30 ml). After adding 1 ml of 50% sodium hydroxide, the basic solution is boiled to coagulate the metallic hydroxides which are then removed by filtration of the hot solution. The filtrate which is collected in a boron-free beaker and acidified with 4 *N* hydrochloric acid is then boiled and titrated as in the carbonate fusion procedure.

A blank determination using benzoic acid in place of the boron compound gave a negligible boron titer.

"Identical pH" method

A 30.5-mg sample of triethanolamine borate was analyzed by the method of WILCOX[6] as further described by TAYLOR[5]. An end-point of pH 6.3 was used.

DISCUSSION

Table I records the analytical results for a variety of aromatic, alkanolamine, and stable boric acid esters. Several esters of lower hydrolytic stability are included to indicate the general applicability of the carbonate fusion procedure for primary, tertiary, polyhalo, olefinic, and carboxyl-containing esters as well.

The procedure led to low results for the alkanolamine esters presumably due to some loss of the sample by sublimation. Both triethanolamine borate and triisopropanolamine borate readily sublime. However, a preliminary treatment with hydrochloric acid followed by the usual procedure resulted in good values for boron. It might be expected that the more volatile aliphatic esters of low molecular weight such as tri-*tert.*-amyl borate (B.p. 235°) similarly would distill before complete reaction with the sodium carbonate and also lead to low results. However, this is not the case and it is possible that the cage-structured alkanolamine esters[3,4] possess a resistance to reaction with sodium carbonate not shared by the other esters. Such unreactivity is consistent with the high hydrolytic stability found for triisopropanolamine borate[3].

The PARR peroxide bomb method which has been used for boron fluoride complexes of esters and ammonia[16] as well as boronic acids[15] has also been applied to the boric acid esters. In general, the method is more time consuming than the carbonate fusion procedure.

It has been found that the carbonate fusion method is useful for various classes of boron-carbon compounds for which the more involved methods of peroxide oxida-

TABLE II

PERCENTAGE BORON IN VARIOUS BORON-CARBON AND BORON-NITROGEN COMPOUNDS

Compound	*Formula*	*Calculated*	*Found*
Triphenylboroxine	$(C_6H_5BO)_3$	10.41	10.37
β-Aminoethyl diphenylborinate	$C_{14}H_{16}ONB$	4.81	4.88
Triphenylborane	$C_{18}H_{15}B$	4.47	4.40
Sodium tetraphenylboron	$C_{24}H_{20}NaB$	3.16	3.15
B-Triphenylborazole	$C_{18}H_{18}N_3B_3$	10.51	10.42
Trisanilinoborane	$C_{18}H_{18}N_3B$	3.77	3.87

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tion[15,17] and mercuric chloride treatment[18,19] are presently used. A variety of boron-nitrogen compounds have also been analyzed successfully (Table II).

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SUMMARY

Boric acid esters of high hydrolytic stability which would require prolonged periods of reflux for hydrolysis and subsequent titration of boric acid can be analyzed conveniently for boron by fusion with sodium carbonate, solution of the melt, and titration of the boric acid in the presence of mannitol. Boric acid esters of phenols or alkanolamines which cannot be analyzed by titration of the boric acid due to the interference of the acidic phenolic or basic amine residues can also be analyzed by the carbonate fusion method. The method has also been applied to esters of primary and tertiary alcohols as well as polyhalo, olefinic, and carboxyl-containing borates. Further applicability to organoboron compounds containing boron-carbon and boron-nitrogen bonds is indicated.

The Parr peroxide bomb method has also been found to be generally applicable for the determination of boron in boric acid esters.

RÉSUMÉ

Une méthode est proposée pour le dosage du bore dans les esters boriques, par fusion au moyen de carbonate de sodium et titrage de l'acide borique en présence de mannitol. Ce procédé peut être appliqué aux organocomposés renfermant des liaisons bore-carbone et bore-azote. On décrit également la méthode au peroxyde de sodium, utilisant une bombe de Parr.

ZUSAMMENFASSUNG

Zur Bestimmung von Bor in Borsäureestern wird der Ester mit Soda geschmolzen und die Borsäure acidimetrisch in Gegenwart von Mannitol titriert. Diese Methode lässt sich auch für Verbindungen mit Bor-Kohlenstoff und Bor-Stickstoff Bindungen anwenden. Der Aufschluss kann auch mit Natriumperoxyd in der Parr Bombe erfolgen.

REFERENCES

[1] A. Scattergood, W. H. Miller and J. Gammon, *J. Am. Chem. Soc.*, 67 (1945) 2150.
[2] J. A. M. van Liempt, *Rec. trav. chim.*, 39 (1920) 38.
[3] H. Steinberg and D. L. Hunter, *Ind. Eng. Chem.*, 49 (1957) 174.
[4] H. C. Brown and E. A. Fletcher, *J. Am. Chem. Soc.*, 73 (1951) 2808.
[5] D. S. Taylor, *J. Assoc. Offic. Agr. Chemists*, 33 (1950) 132.
[6] L. V. Wilcox, *Ind. Eng. Chem., Anal. Ed.*, 4 (1932) 38.
[7] T. Ahmed, S. Z. Haider and M. H. Khundkar, *J. Appl. Chem.*, 4 (1954) 543.
[8] A. Pictet and A. Geleznoff, *Ber.*, 36 (1903) 2219.
[9] L. H. Thomas, *J. Chem. Soc.*, (1946) 820, 823.
[10] E. T. Wherry and W. H. Chapin, *J. Am. Chem. Soc.*, 30 (1908) 1687.
[11] W. W. Scott, *Standard Methods of Chemical Analysis*, 5th Ed., D. Van Nostrand Co., Inc., New York 1947, p. 164.
[12] A. Rosenheim and H. Vermehren, *Ber.*, 57 (1924) 1337.
[13] H. Roth, *Angew. Chem.*, 50 (1937) 593.
[14] D. F. Kuemmel and M. G. Mellon, *J. Am. Chem. Soc.*, 78 (1956) 4572.
[15] H. R. Snyder, J. A. Kuck and J. R. Johnson, *J. Am. Chem. Soc.*, 60 (1938) 105.
[16] D. J. Pflaum and H. H. Wenzke, *Ind. Eng. Chem.*, 4 (1932) 392.
[17] R. B. Booth and C. A. Kraus, *J. Am. Chem. Soc.*, 74 (1952) 1415.
[18] K. Torssell, *Acta Chem. Scand.*, 8 (1954) 1779.
[19] G. Wittig, G. Keicher, A. Ruckert and P. Raff, *Ann.*, 563 (1949) 110.

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RAPID DETERMINATION OF THORIUM IN ORES

III. DETERMINATION OF MICROGRAM AMOUNTS OF THORIUM IN ILMENITE SANDS

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It was necessary in certain projects to know exactly the residual monazite content in ilmenite sands and therefore, to determine thoria in ilmenite when less than 0.015% was present. In an earlier communication[1] from this laboratory a method was described for the determination of more than 0.01% of thoria in minerals and ores.

Thorin[2] has been used for the colorimetric determination of thorium by many workers. As it is not specific a preliminary separation of thorium has to be carried out. BANKS AND BYRD[3] separated milligram and higher amounts of thorium from monazite by extracting with mesityl oxide from a solution of thorium fluoride in aluminium nitrate. CLINCH[4] carried out a similar separation with oxalate at a controlled pH of 4 and with calcium as carrier. Recently GRIMALDI *et al.*[5] have developed a method for selective precipitation of thorium as iodate in presence of tartaric acid and hydrogen peroxide. The method was used for the determination of thorium in silicate rocks and of 0.01% of thoria or more in black sands. The method followed in this laboratory[1] has now been modified to determine less than 0.05% of monazite in ilmenite sands.

PRINCIPLE

The ilmenite is opened up with sodium peroxide and thorium precipitated as hydroxide with ammonia without prior removal of silica. Silica is removed by volatilisation in hydrofluoric acid and thorium collected as fluoride with lanthanum. The fluorides are decomposed with sulphuric acid and finally taken up in 10% nitric acid. Thorium is precipitated as iodate with mercuric nitrate as carrier. Thorium is finally determined spectrophotometrically, with thorin as the colorimetric reagent.

Reagents

Mercuric nitrate: 1.58 g of mercuric nitrate (E. Merck) dissolved in 10 ml of (1:1) nitric acid and diluted to 1 litre (1 ml = 1 mg of HgO). Oxalic acid: 10% oxalic acid solution. Hydrogen peroxide: 10 ml of 30% H_2O_2 diluted to 100 ml with distilled water. Lanthanum nitrate: To contain 1 ml = 1 mg La_2O_3 in dilute HNO_3. Hydrofluoric acid wash solution: 5 ml of HF diluted to 100 ml with distilled water. Potassium iodate reagent: 15 g of KIO_3 (E. Merck) dissolved in 100 ml of HNO_3 (1:1) and filtered through a dry paper. Potassium iodate wash solution: 10 g of KIO_3 dissolved in 200 ml of HNO_3 (1:1) and made up to 1 litre with distilled water. Thorin reagent: 0.1 g of thorin (Eastman Kodak) dissolved in distilled water and made up to 100 ml. Standard thoria solution: 1 ml = 5 μg of thoria.

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The standard curve

Aliquots of standard thorium nitrate solution were taken containing 5 to 100 µg of thoria. 2 ml of nitric acid were added and the volume made up to 16 ml. The thorium was precipitated as iodate in presence of oxalic acid with mercuric iodate as carrier. After washing and decomposing the iodates, thorin was added and the optical densities were measured against a blank taken through the same procedure. (Details are given below). Beer's law was obeyed from 5 to 100 µg of thorium (Table 1).

TABLE I

OPTICAL DENSITIES OF STANDARD THORIUM SOLUTION

(5 to 100 µg) with thorin and 5 mg of mercuric oxide as carrier, against reagent blank

No.	*Thorium oxide (µg) taken*	*Optical density against blank with standards taken directly*	*Optical densities against blank and standards run through the procedure*
1.	5.00	0.008	0.008
2.	10.00	0.017	0.017
3.	20.00	0.035	0.035
4.	40.00	0.066	0.065
5.	60.00	0.107	0.107
6.	80.00	0.138	0.139
7.	100.00	0.180	0.182

Procedure

A 1-g sample was cautiously fused in a nickel crucible with 5–6 g of sodium peroxide, the mass being kept liquid for about 10 min. The crucible was cooled and transferred to a 250-ml beaker. About 100 ml of cold water were added and the melt was disintegrated. The crucible was removed and rinsed first with water and then with hydrochloric acid (1:1).

The solution was neutralized with (1:1) hydrochloric acid and then 10 mg of zirconium oxide were added as the nitrate. (If titanium or zirconium are present in the sample, which can be noticed from the ammonia precipitate, it is not necessary to add zirconium.) The solution was warmed to about 90° and ammonia was added in excess to give a precipitate. The contents of the beaker were then digested on a water bath for 30 min.

The solution was filtered on a Whatman No. 540, 11 cm paper, and the precipitate washed with the ammonia wash solution. The precipitate was then transferred to a 100-ml platinum dish. The paper was burned in a platinum crucible and the ash added to the dish. 20 ml of hydrofluoric acid were added and the mixture was digested on a steam bath, while stirring with a platinum rod, and evaporated to about 8 ml. 10 ml of hydrofluoric acid were then added and the solution was re-evaporated to about 8 ml and then diluted with 30 ml of water. The solution was warmed on the steam bath and 10 mg of lanthanum oxide in the form of nitrate were added. The solution was stirred with a platinum rod and allowed to stand overnight at room temperature.

The solution was filtered on a Whatman No. 40, 9 cm filter paper in a hard rubber or plastic funnel. The precipitate was washed twice with 10 to 15 ml of 5% hydrofluoric acid wash solution and then twice with water.

The paper and the precipitate were transferred back to the dish and carefully charred but not ignited. When fumes were no longer evolved the contents were heated at 600° until carbon was burnt off. The residue was carefully moistened with a few drops of water, 0.5 ml of sulphuric acid and one drop of hydrofluoric acid. The dish was heated on the hot plate for about 25 min until dry and then over a low Bunsen flame below 450° until no more fumes appeared. 15 ml of conc. nitric acid were added and the solution was evaporated to dryness on the water bath. This was repeated two or three times, until all the thorium was in solution. 2 ml of (1:1) nitric acid and 5 ml of water were added to dissolve any residue and the solution was filtered through Whatman No. 42, 7 cm paper. The final volume of the solution in beaker was about 16 ml. To the solution, 5 drops of hydrogen peroxide, 0.5 ml of oxalic acid and 5 mg of mercuric oxide as the nitrate were added and thorium precipitated as iodate with 3 ml of potassium iodate solution. The beaker was placed in cold water overnight to ensure complete precipitation.

The precipitate was filtered through Whatman No. 541, 7 cm paper, being transferred with the potassium iodate wash solution, and washed four times with the wash solution. It was then washed back into the beaker with distilled water. The paper was washed with a mixture of hydrochloric acid and sulphurous acid until all the iodate had decomposed and no stains of iodine remained on the paper. The solution was evaporated and fumed with 1 ml of perchloric acid to dryness. 0.5 ml of hydrochloric acid and 20 ml of distilled water were then added and the mixture was heated on the water bath until all the residue was in solution. 3 ml of 0.1% thorin were added and volume made up to 25 ml.

After 30 min, the optical densities of the solutions were measured on a Beckman DU quartz spectrophotometer at 545 mμ with a 1-cm cell against a blank which had been similarly treated. The thoria present in the sample was calculated from the standard curve.

Application of the method for the determination of thoria in ilmenite sands

In order to check the procedure, the recoveries of thorium added to ilmenite were determined. As no ilmenite containing thoria of the order of 0.001% was available, an artificial ilmenite was prepared containing about 40% FeO and 60% TiO_2. To a 1-g sample 10 to 50 μg of thoria were added and thorium was determined as given above. It was found that 1 g of the artificial sample contained about 8 μg of thoria and that the recoveries of added thoria were quantitative (Table II).

TABLE II

RECOVERIES OF ADDED THORIA (10 TO 50 μg) TO AN ARTIFICIAL ILMENITE, THROUGH THE ENTIRE PROCEDURE

No.	*Artificial ilmenite taken*	*Thoria added μg*	*Thoria recovered μg*	*Remarks*
1.	1.000	—	8	8 μg of thoria were found in 1 g of the artificial ilmenite
2.	1.000	10	17	
3.	1.000	20	27	
4.	1.000	40	46	
5.	1.000	50	54	

Thoria was then determined in three mixtures of ilmenite and monazite (Table III).

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TABLE III

DETERMINATION OF THORIA IN SYNTHETIC MIXTURES OF ILMENITE AND MONAZITE

No.	*Nature of sample*	*Wt. of sample taken g*	*Thoria*		*Remarks*
			Expected %	*Found %*	
1.	Ilmenite (A)	1.000	—	0.0078	Mean of 3 readings
2.	Ilmenite (A) + Monazite (B) 99.950% + 0.050%	0.500	0.0119	0.0110	Mean of 2 readings
3.	Ilmenite (A) + Monazite (B) 99.900% + 0.099%	0.500	0.0159	0.0150	Mean of 3 readings
4.	Ilmenite (A) + Monazite (B) 99.850% + 0.15%	0.500	0.0201	0.0200	Mean of 3 readings
5.	Ilmenite (B)	0.100	—	0.053	Value by trace method[1] = 0.052%

Monazite (B) contains 8.20% thoria.

The results show that the recoveries of thoria agree fairly well and that it is possible to estimate less than 0.05% of monazite in ilmenite samples.

SUMMARY

A previous method has been modified to determine less than 0.05% of monazite in ilmenite samples, with thorin as the colorimetric reagent; mercuric iodate serves as carrier.

RÉSUMÉ*

Les auteurs proposent une modification de leur méthode utilisant l'iodate mercurique comme entraîneur. On peut ainsi déterminer, dans des échantillons d'ilménite, des teneurs en monazite inférieures à 0.05%. On utilise le thorin comme réactif colorimétrique.

ZUSAMMENFASSUNG

Es wird über eine Modifikation der früher beschriebenen Methode zur Bestimmung von Monazit in Ilmenit berichtet. Mit Quecksilber(II)-jodat als Trägersubstanz lassen sich weniger als 0.05% Monazit bestimmen, wobei Thorin als colorimetrisches Reagenz verwendet wird.

REFERENCES

[1] M. M. Tillu and V. T. Athavale, *Anal. Chim. Acta*, 11 (1954) 324.
[2] P. F. Thomson, M. A. Perry and W. M. Byerly, *Anal. Chem.*, 21 (1949) 1239.
[3] C. V. Banks and C. H. Byrd, *Anal. Chem.*, 25 (1953) 416.
[4] J. Clinch, *Anal. Chim. Acta*, 14 (1956) 162.
[5] F. S. Grimaldi, L. B. Jenkins and M. H. Fletcher, *Anal. Chem.*, 29 (1957) 848.

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ANALYSIS OF SILVER SOLDERS BY ANION EXCHANGE AND EDTA TITRATION

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The recent pioneering work of Kraus and Nelson[1] on the anion exchange of metal chloride complexes with quaternary-amine type resins has opened a broad new field for metal separations. In the author's laboratory, it has been found that the anion-exchange separation of nickel, copper, zinc, and cadmium may be combined quite conveniently with the titration of these elements by the disodium salt of (ethylenedinitrilo)tetraacetic acid (EDTA). As one or more of the above elements often occur along with silver in most commercial silver solder alloys, a procedure for their analysis by these techniques is presented.

In the procedure to be described, silver is first determined in dilute nitric acid solution by potentiometric titration with chloride. The solution is then prepared for anion-exchange chromatography by filtration and addition of the proper amount of hydrochloric acid. After adsorption on the column, the anions are eluted by washing the resin column with successively more dilute solutions of hydrochloric acid. Although zinc and cadmium may be titrated directly with EDTA in their respective eluates, it is necessary to evaporate the nickel and copper eluates to dryness on the steam bath first to rid them of their large excess of hydrochloric acid.

Whereas the anion-exchange separations reported in this present paper depend largely upon the original work of Kraus and Nelson[1], others such as Berg and Truemper[2], Kallmann, Oberthin, and Lin[3] and Jackson[4] have applied anion exchange to the separation of two or more of the elements considered here.

APPARATUS AND REAGENTS

Standard glass chromatographic tubes commercially available (Fisher Scientific Co. #5-722) and measuring about 30 cm in length by 1.0 cm internal diameter were used. Each tube was filled to a height of 20 cm with about 10–12 grams of the anion-exchange resin Dowex 1-8X, 100 to 200 mesh, introduced as a water slurry. The liquid holdup of each column was about 9.5 ml.

A Beckman Model H-2 pH meter was used for the potentiometric titration of silver with chloride ion. A saturated calomel electrode and 1 *M* potassium nitrate-agar salt bridge were used as the reference electrode, pure silver wire as the other electrode.

Zinc and cadmium of "super purity" spectrographic grade, high purity nickel foil, electrolytic copper wire, and carefully dried reagent grade silver nitrate were used as standards. Other chemicals were the usual reagent or C.P. grades. EDTA (0.1 *M*) was standardized against zinc using Eriochrome Black T as indicator, and against copper using murexide as indicator.

Buffer of pH 9.2 used in the titration of zinc and cadmium was prepared from ammonium chloride and ammonium hydroxide so that the resulting solution was 0.5 *M* in each.

Zinc EDTA was prepared by the titration of a solution containing about 1% of zinc chloride with EDTA to its equivalence point. This solution was buffered with about 10 ml of pH 9.2 buffer and Eriochrome Black T was used as the indicator.

PROCEDURE

About 200 mg of sample are dissolved in a few ml of 8 *M* nitric acid, and the solution is evaporated just to dryness on the steam bath. The residue is then dissolved in about 10 ml of water and titrated potentiometrically with standard 0.1 *N* hydrochloric acid.

The silver chloride precipitate is now removed by filtration, care being taken to keep the wash water below a final volume of 45 ml.

If nickel is present in the filtrate, the filtrate should be made approximately 6 *M* in hydrochloric acid by the addition of an equal volume of conc. hydrochloric acid. If only copper, zinc, and cadmium are present, one eleventh volume of concentrated hydrochloric acid is added to the filtrate to make it 1 *M* in hydrochloric acid. The anion-exchange column is readied by a preliminary wash with a few ml of 6 *N* or 1 *N* hydrochloric acid as required, and the solution containing the unknown is introduced into the top of the column as soon as it has run dry. A reservoir on top of the chromatographic tube is quite helpful here. With 100–200 mesh resin, there is no danger of air being drawn into the interstitial spaces of the column if it should accidently run dry. A final wash with 25 ml of 6 *N* hydrochloric acid serves to flush the nickel out of the interstitial spaces of the column without disturbing the other elements adsorbed on the resin.

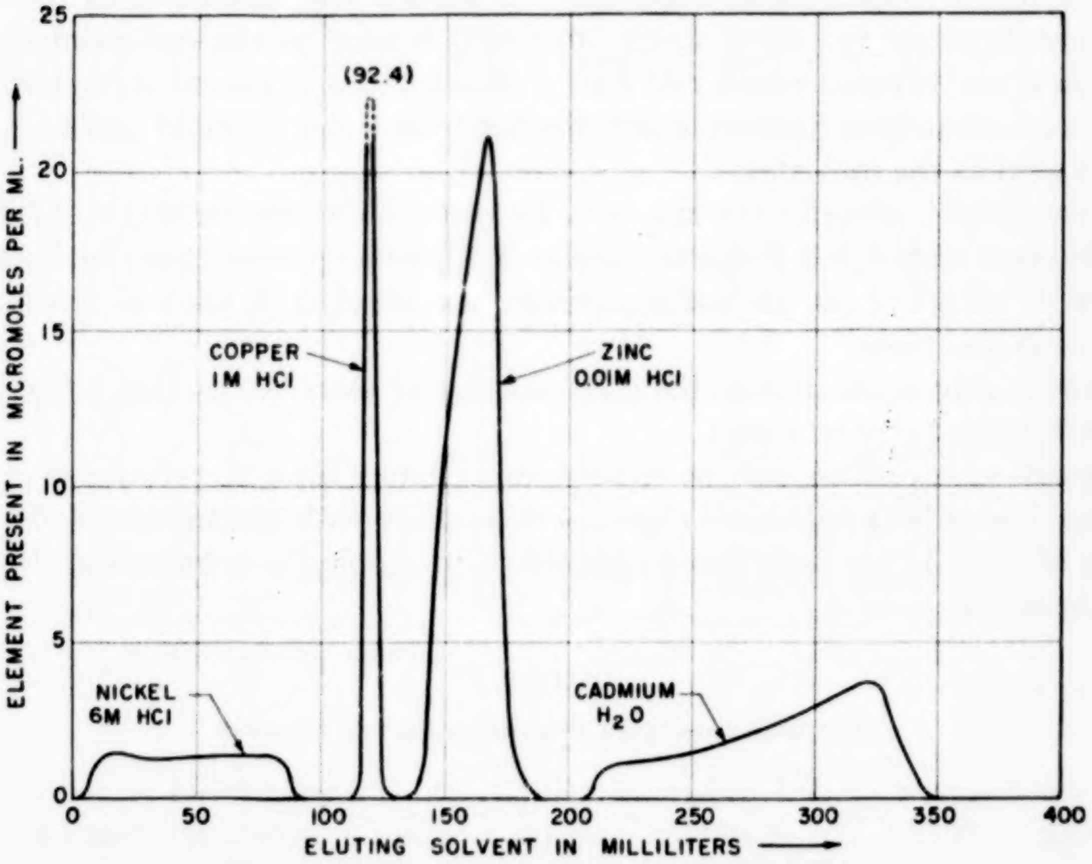

Fig. 1. Elution curves of Ni, Cu, Zn and Cd.

Copper may be eluted from the column with 30 ml of 1 *N* hydrochloric acid. Zinc is eluted with 70 ml of 0.01 *N* hydrochloric acid, and the cadmium is finally eluted by a wash with 180 ml of water.

The progress of a typical elution is shown by the curves of Fig. 1, where small fractions were separately collected and analyzed. Here it can be seen that in 6 N hydrochloric acid nickel passes quickly through the column, while copper, zinc, and cadmium are adsorbed. Copper is rapidly eluted by 1 N hydrochloric acid, however, while zinc and cadmium are completely eluted by 0.01 N hydrochloric acid and water respectively.

If nickel is absent, of course, one may proceed directly to the 1 N hydrochloric solution, and copper will pass through the column without adsorption.

The EDTA titration of the above eluates are carried out by methods already available in the literature[5], with slight modification where necessary or expedient.

The eluates that contain the nickel and copper should first be evaporated to dryness on the steam bath because of the deleterious effect of a high concentration of ammonium salts on the murexide indicator. The nickel residue is dissolved in about 10 ml of concentrated ammonium hydroxide and titrated with EDTA after dilution with about 150 ml of water. Murexide is used as the end-point indicator.

Copper is also titrated with 0.1 M EDTA after solution of the dried residue in about 5 ml of 4 N ammonium hydroxide and dilution with water to about 300 ml murexide again is used as the indicator.

The eluate that contains the zinc may be titrated directly for zinc by EDTA after neutralization with a few drops of sodium hydroxide or ammonium hydroxide and addition of 10 ml of pH 9.2 buffer. Eriochrome Black T is used as the end-point indicator in this case.

Cadmium may be titrated in the same manner as zinc, except that a few drops of zinc EDTA must also be added.

Although each column may be re-used immediately after the elution of cadmium, a gradual loss of both speed and capacity takes place with continued use of the same column of resin. It has been found desirable to recharge the column with fresh resin after about four uses.

TABLE I

RECOVERY DATA ON SYNTHETIC SILVER SOLDERS

Sample No.	*Element*	*Mg present*	*Mg found*			
			A	*B*	*C*	*Mean*
1	Ag	100	99.6	100.0	100.1	99.9
	Ni	6	6.5	6.2	6.1	6.3
	Cu	31	31.1	31.0	30.9	31.0
	Zn	31	30.9	31.1	31.0	31.0
	Cd	32	32.3	32.5	32.5	32.4
2	Ag	90	90.3	90.1	—	90.2
	Cu	30	30.4	29.9	—	30.2
	Zn	32	32.0	32.0	—	32.0
	Cd	48	48.0	48.0	—	48.0
3	Ag	100	100.0	99.4	—	99.7
	Cu	68	—	67.8	—	67.8
	Zn	32	32.1	31.9	—	32.0
4	Ag	30	29.5	29.5	—	29.5
	Cu	160	159.7	159.5	—	159.6
	P	10				

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RESULTS

In Table I are the results obtained by this procedure on synthetic alloys prepared by weighing the pure metals and silver nitrate as required. A comparison of the results obtained by this procedure and those obtained by the more conventional ASTM methods is presented in Table II. Agreement between the methods is felt to be adequate.

TABLE II

COMPARISON OF ANION EXCHANGE AND ASTM METHODS ON UNKNOWN SILVER SOLDERS

Sample No.	*Element*	*Anion exchange-EDTA %*			*ASTM %*
		A	*B*	*Mean*	
1	Ag	25.76	25.57	25.67	25.64
	Ni	1.65	1.66	1.66	1.65
	Cu	56.99	56.88	56.94	56.70
	Zn	8.27	8.24	8.26	8.05
	Cd	7.86	7.85	7.86	7.93
	Total	100.53	100.20	100.39	99.97
2	Ag	44.84	44.75	44.80	44.83
	Cu	14.90	15.04	14.97	15.04
	Zn	15.87	15.82	15.85	
	Cd	24.46	24.35	24.41	24.51
	Total	100.07	100.06	100.03	
3	Ag	49.88	50.02	49.95	49.69[a]
	Cu	34.06	34.10	34.08	32.24[a]
	Zn	15.96	15.94	15.95	15.98[a]
	Total	99.90	100.06	99.98	99.91[a]

[a] Mean of two values.

ACKNOWLEDGEMENTS

The author is indebted to B. H. KINDT for many helpful suggestions, and to R. B. NORTHROP for chemical analysis of silver solders by the ASTM methods.

SUMMARY

The separation of nickel, copper, zinc, and cadmium by anion-exchange chromatography has been found to be particularly suitable for the analysis of most commercial silver solders. After solution of the sample, the silver is separated by precipitation as the chloride. The components in the filtrate are separated as their chloro complexes by passage through an anion-exchange column and titrated in the eluates with EDTA. Results compare favorably with those obtained by the more conventional ASTM methods.

RÉSUMÉ

La séparation nickel, cuivre, zinc et cadmium par chromatographie d'échange d'anions convient particulièrement bien à l'analyse de la plupart des soudures d'argent du commerce. Après séparation de l'argent comme chlorure, les autres cations, sous forme de chlorocomplexes, sont séparés sur colonne d'échange d'anions et titrés ensuite par l'acide éthylènediaminotétracétique.

ZUSAMMENFASSUNG

Die Trennung von Nickel, Kupfer, Zink und Cadmium nach dem Verfahren der Ionenaustauscher-Chromatographie hat sich als besonders geeignet erwiesen für die Analyse der meisten

Silberlote des Handels. Nach Abtrennung des Silbers als Silberchlorid werden die übrigen Kationen in Form der Chloro-Komplexe mit Hilfe einer Anionenaustauscherkolonne getrennt und in den Eluaten mit Aethylendiaminotetraessigsäure titriert.

REFERENCES

[1] K. A. Kraus and F. Nelson, *Proc. Intern. Conf., Peaceful Uses Atomic Energy,* Geneva 1955, 7 (1956) 113.
[2] E. W. Berg and J. T. Truemper, *Anal. Chem.*, 30 (1958) 1827.
[3] S. Kallmann, H. Oberthin and R. Lin, *Anal. Chem.*, 30 (1958) 1846.
[4] E. Jackson, *Metallurgia*, 56 (1957) 307.
[5] F. J. Welcher, *The Analytical Uses of Ethylenediamine Tetraacetic Acid*, D. Van Nostrand Co., Inc. New York 1958.

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COULOMETRIC TITRATION WITH HIGHER OXIDATION STATES OF MANGANESE

ELECTROLYTIC GENERATION AND STABILITY OF +3 MANGANESE IN SULFURIC ACID MEDIA

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Quite recently Tutundžić and Mladenović[1] introduced the use of electro-oxidized manganese solutions for the coulometric titration of such reductants as +2 iron, +3 arsenic, and oxalic acid. They concluded that permanganate ion is produced by electro-oxidation at a platinum anode of solutions containing 0.02 to 0.45 M manganous sulfate in 1.8 M or higher concentrations of sulfuric acid. They appear to have based this conclusion merely on the red-violet color of the oxidized solutions and the fact that the oxidation potential of the solutions is in the vicinity of that of the permanganate ion–manganous ion couple. However, visual observation is unreliable because +3 manganese in sulfuric acid has a color quite similar to that of permanganate ion. Furthermore the potential of the +3/+2 manganese couple happens to be nearly the same as that of the permanganate–manganous ion couple, and hence cannot be used to distinguish the species present in the solutions.

That the solution, electro-oxidized under the conditions used by Tutundžić and Mladenović[1], does not contain permanganate is clearly evident from the absorption spectra shown in Fig. 1.

The work of Sem[2], Campbell[3], Grube and Huberich[4], and Vetter and Manecke[5], suggests +3 manganese as the most likely species in solutions electro-oxidized under the conditions specified by Tutundžić and Mladenović[1]. This has

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been confirmed in the present study. We have also investigated the equilibrium between +2, +3 and +4 manganese over a range of sulfuric acid concentrations, and evaluated the current efficiency for the electro-oxidation of +2 manganese to the +3 state at a platinum anode as a function of sulfuric acid concentration, +2 manganese concentration and current density.

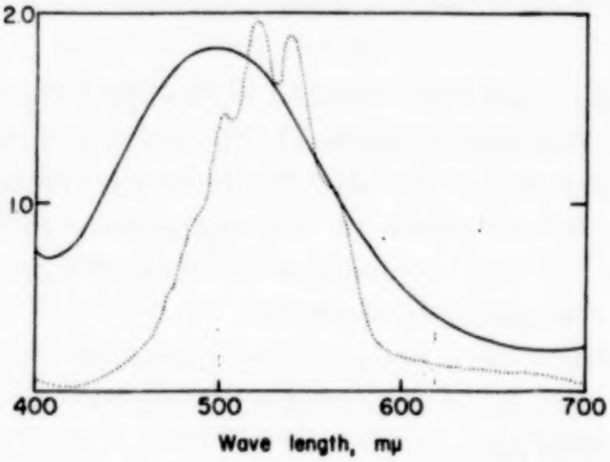

Fig. 1. Comparison of the absorption spectrum of 0.87 m*M* permanganate ion in 1 *M* sulfuric acid (dotted line) with that of +3 manganese (solid line). The +3 manganese solution was prepared by electrooxidizing 100 ml of a 0.2 *M* manganous sulfate solution in 7 *M* sulfuric acid for 5800 sec with a current of 24.8 mA.

Equilibrium between +2, +3 and +4 manganese in sulfuric acid solution

For the disproportionation reaction:

$$2\ \mathrm{Mn}^{+3} \rightleftharpoons \mathrm{Mn}^{+2} + \mathrm{Mn}^{+4} \quad (1)$$

the formal equilibrium constant has the form:

$$K = \frac{[\mathrm{Mn}^{+2}]\,[\mathrm{Mn}^{+4}]}{[\mathrm{Mn}^{+3}]^2} \quad (2)$$

In this study absorption spectrophotometry was used to determine the formal equilibrium constant, whose value varies from 10^{-3} in 4 *M* sulfuric acid to 10^{-4} in 7.2 *M* sulfuric acid. These values are about one-tenth those previously reported by GRUBE AND HUBERICH[4], and VETTER AND MANECKE[5], in studies using potentiometric measurements.

In order to determine the equilibrium constant spectrophotometrically it was necessary to evaluate the spectra of the various species of manganese involved in the equilibrium. The absorption spectrum of +2 manganese is easily obtained. Indeed, the extinction coefficient of this species is so small over the range of wave lengths at which measurements were made in this study that its contribution to the total absorbance can be neglected.

To obtain the absorption spectrum of +3 manganese, solutions of this species were prepared by the direct oxidation of +2 manganese with permanganate in strong sulfuric acid solutions. Fig. 2 shows a spectrophotometric titration curve of +2 manganese in 6.3 *M* sulfuric acid with a standard solution of potassium permanganate. The end-point corresponds closely to the reaction:

$$Mn^{+7} + 4\ Mn^{+2} = 5\ Mn^{+3} \quad (3)$$

The reaction is quite rapid, as indicated by the fact that constant values of the absorbance are obtained almost immediately on addition of the permanganate titrant. The deviation from linearity of the absorbance in the region close to the end-point results from the disproportionation of +3 manganese. Prior to the end-point the solution contains only +2 and +3 manganese in significant concentrations, and the concentration of +4 manganese is negligible.

Because +2 manganese does not absorb significantly, the extinction coefficient, ε_3, of +3 manganese can be evaluated from the observed absorbance, *A*, prior to the end-point by the relation:

$$A = \varepsilon_3[Mn^{+3}] \quad (4)$$

Although the titration is fairly exact, there is nonetheless some reduction of permanganate by water concommitantly with its reduction by +2 manganese. Therefore

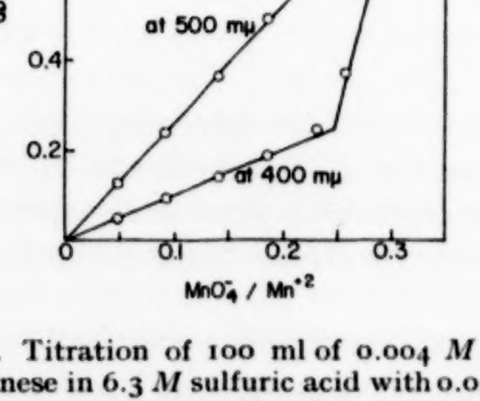

Fig. 2. Titration of 100 ml of 0.004 *M* +2 manganese in 6.3 *M* sulfuric acid with 0.02 *M* permanganate solution. Absorbance, corrected for volume change, was measured with a Beckman Model DU spectrophotometer using 1-cm silica cells. The abscissa represents the ratio of the moles of permanganate added to the moles of +2 manganese initially present.

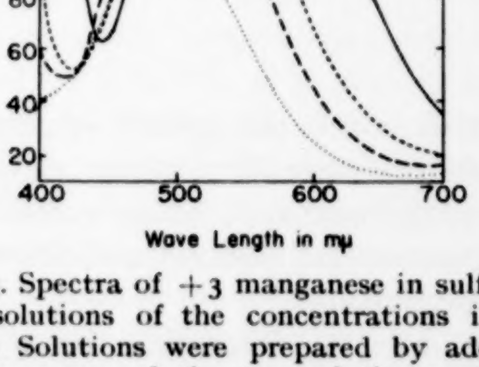

Fig. 3. Spectra of +3 manganese in sulfuric acid solutions of the concentrations indicated. Solutions were prepared by adding permanganate solution to a solution containing a large excess of +2 manganese. The exact concentration of +3 manganese resulting from the reaction was determined by titration with ferrous ion immediately after recording the spectrum with a Cary Recording Spectrophotometer.

the concentration of +3 manganese was evaluated by reductometric titration with ferrous ion, which is more accurate than its evaluation by calculation from the volume of permanganate added.

Fig. 3 shows the spectrum of +3 manganese, determined in this fashion, at a number of sulfuric acid concentrations. All spectra were obtained in solutions where the concentration of +2 manganese was at least ten times that of the +3 species. The spectra of solutions electro-oxidized under the conditions specified by TUTUNDŽIĆ AND MLADENOVIĆ[1] are identical with the spectrum of +3 manganese obtained by direct oxidation of +2 manganese with permanganate.

After the end-point in the titration shown in Fig. 2, the addition of permanganate results in oxidation of +3 manganese to the +4 state. That +4 manganese is indeed the product of this further oxidation is inferred from the fact that the absorbance at 500 mμ is too small, and the absorbance at 410 mμ too large, to be ascribed only to the excess permanganate added. In view of the known high degree of instability of +5 and +6 manganese in acid solutions, it is assumed that neither of these species is present in significant concentration.

However, one cannot obtain a second end-point in the titration, corresponding to complete oxidation of +3 manganese to the +4 state. This is prevented by the competition between the reduction of permanganate by water and by +3 manganese according to:

$$Mn^{+7} + 3\,Mn^{+3} = 4\,Mn^{+4} \qquad (5)$$

$$Mn^{+7} + 2\,H_2O = Mn^{+3} + O_2 + 4\,H^+ \qquad (6)$$

The following rate expression for the reduction of permanganate agrees relatively well with the observed data:

$$-\frac{d\,[MnO_4^-]}{dt} = k_1[MnO_4^-] + k_2[MnO_4^-]\,[Mn^{+3}] \qquad (7)$$

Shortly after the end-point of the titration shown in Fig. 2, when the concentration of +3 manganese is relatively high, reaction (5) is the predominant reaction. As the concentration of this species becomes less, reaction (6) predominates.

To obtain the spectrum of +4 manganese, solutions containing known concentrations of +3 and +4 manganese were prepared. By subtracting from the absorption spectra of such solutions the contribution of +3 manganese to the absorption, one obtains the spectrum of the +4 species.

For the preparation of solutions containing a mixture of +3 and +4 manganese the following procedure was followed. A standard solution of potassium permanganate (*ca.* 0.02 *M*) was added dropwise to exactly half its volume of concentrated sulfuric acid, with vigorous stirring in an ice bath. The final concentration of sulfuric acid was 6.3 *M*. This solution was then diluted to an appropriate volume with 6.3 *M* sulfuric acid, to give a solution in which the concentration of total manganese was between 0.002 to 0.0065 *M*. The solution was then allowed to stand at room temperature for at least 36 h. During this period there was a rapid change in the spectral properties of the solution and a concomitant loss of oxidizing titer. After this period a brown colored solution was obtained, the spectrum and oxidizing titer of which then remained relatively constant.

The results of a spectrophotometric titration of this brown-colored solution with both ferrous ion and with +2 manganese are shown in Fig. 4. Titration with +2 manganese results only in the reduction of +4 manganese to the +3 state. In the titration with ferrous ion the +4 manganese is first reduced to the +3 state and then to the +2 state. The fraction of manganese in the original solution existing in the +4 state is the ratio of the volume of ferrous ion required to reach the first end-point to the volume required to go from the first to the second end-point.

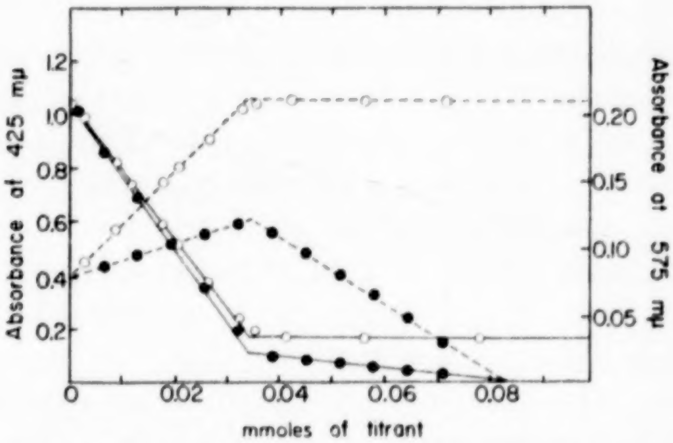

Fig. 4. Titration of solution obtained by allowing 0.0494 mmoles of permanganate contained in 25 ml of 6.3 *M* sulfuric acid to stand for 36 h. Solid circles represent titration with 0.0129 *N* ferrous ion, open circles represent titration with 0.00296 *M* +2 manganese. Solid line represents absorbance at 425 m*μ*, and the dotted line represents absorbance at 575 m*μ* measured in 1-cm silica cell.

In the early part of the titration where the linearity of absorbance indicates that the disproportionation of +3 manganese has been repressed by the +4 manganese present, the solutions contain essentially only +3 and +4 manganese with only a negligible amount of the +2 species, and the extinction coefficient of +4 manganese at a particular wave length can be calculated from:

$$[\mathrm{Mn}] = [\mathrm{Mn}^{+3}] + [\mathrm{Mn}^{+4}] \qquad (8)$$

$$[\mathrm{Ox}] = [\mathrm{Mn}^{+3}] + 2\,[\mathrm{Mn}^{+4}] \qquad (9)$$

$$A = \varepsilon_3[\mathrm{Mn}^{+3}] + \varepsilon_4[\mathrm{Mn}^{+4}] \qquad (10)$$

in which [Mn] is the total concentration of manganese and [Ox] is the oxidizing titer as determined by titration with ferrous ion. In Fig. 5 the spectrum of +4 manganese determined in this way is shown, together with the spectra of +3 manganese and permanganate for comparison.

Knowing the extinction coefficients of +3 and +4 manganese and permanganate at a particular wave length, it is then possible to calculate the concentrations of these three species during the course of decomposition of permanganate in sulfuric acid solution. These concentrations were calculated from data on the variation of absorbance and oxidizing titer with time, together with the value for the total manganese concentration. Fig. 6 presents the results of such a calculation.

The final composition of the solutions depends on the initial concentration of permanganate. Solutions initially 0.002 *M* in permanganate give a final composition in which 70% of the manganese exists in the +4 state and 30% in the +3 state. Solutions initially 0.0065 *M* in permanganate give a final composition in which 90% of the manganese exists in the +4 state and 10% in the +3 state.

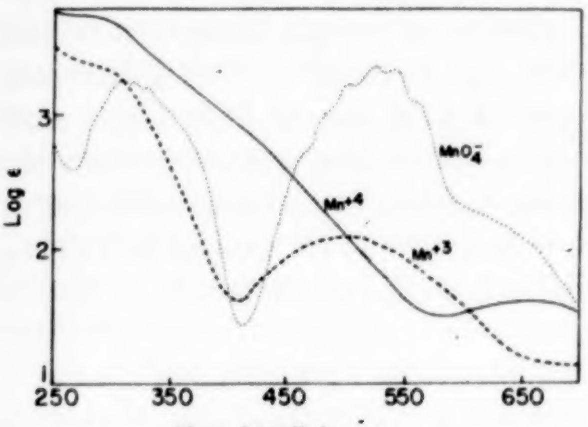

Fig. 5. Spectra of +3 and +4 manganese in 6.3 *M* sulfuric acid, and permanganate in neutral aqueous solution.

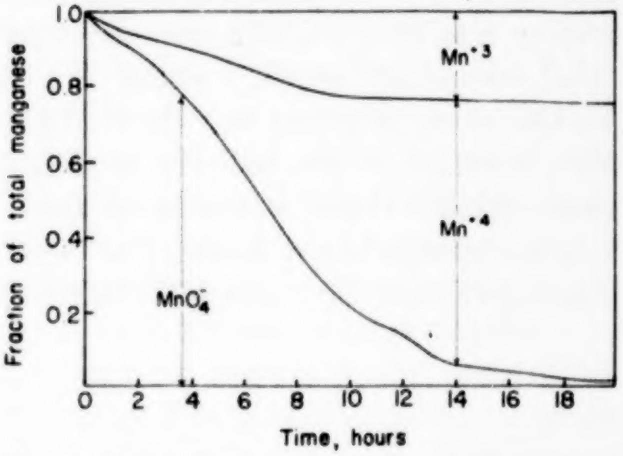

Fig. 6. Rate of decomposition of permanganate, initially 0.002 *M*, in 6.3 *M* sulfuric acid at room temperature.

After three or four months a precipitate formed in which the average oxidation number of manganese was +3.7. In the more dilute solutions the precipitate formed a tightly adherent film on the walls of the vessel, while the solution itself remained clear. In the more concentrated solutions the precipitate formed in the solution itself. This precipitate probably is a non-stoichiometric mixture of oxides of +3 and +4 manganese.

It appears that +4 manganese does not exist in these solutions in the colloidal state. This is inferred both from the fact that no Tyndall effect is exhibited by solutions containing large concentrations of +4 manganese and from chronopotentiometric measurements, which indicate that the diffusion coefficients for both +3 and + 4 manganese are about equal (*ca.* $0.2 \cdot 10^{-5}$ cm²/sec) in 6.3 *M* sulfuric acid.

In 6.3 *M* sulfuric acid the decomposition of +3 and +4 manganese via reduction by water is quite slow. The half life for +4 manganese is about 2 months, while the half-life for +3 manganese is about 30 months. In solutions of both higher and lower acid concentrations decomposition of +3 and +4 manganese is more rapid.

When all three species are present in significant concentrations (the situation which obtains in the region close to the first end-point) the complete system of equations describing the system is:

$$K = \frac{[Mn^{+2}]\,[Mn^{+4}]}{[Mn^{+3}]^2}$$

$$[Ox] = [Mn^{+3}] + 2\,[Mn^{+4}]$$

$$A = \varepsilon_3[Mn^{+3}] + \varepsilon_4[Mn^{+4}]$$

$$[Mn] = [Mn^{+2}] + [Mn^{+3}] + [Mn^{+4}]$$

Knowing the extinction coefficients of +3 and +4 manganese, this system of equations can be solved for K, the formal disproportionation constant. Maximum accuracy will be obtained when measurements are made exactly at the first end-point, where $[\mathrm{Mn}] = [\mathrm{Ox}]$ and $[\mathrm{Mn}^{+2}] = [\mathrm{Mn}^{+4}]$.

The procedure for the determination of the equilibrium constant consisted in titrating an aliquot of the solution of +3 and +4 manganese, obtained by the decomposition of permanganate, with +2 iron to determine [Ox]. To a second aliquot was then added a volume of a standard solution of +2 manganese such that [Mn] was made exactly equal to [Ox], and the absorbance, A, was measured. To the same solution was then added an amount of solid $MnSO_4 \cdot H_2O$, such that after solution of this salt the concentration of total manganese was more than ten times greater than the oxidizing titer. Under these conditions the concentration of +4 manganese is negligible. The measured absorbance, $A°$, is then equal to $\varepsilon_3[\mathrm{Ox}]$. The expression for the equilibrium constant then takes the simple form:

$$K = \frac{(A/A^\circ) - 1}{(\varepsilon_4/\varepsilon_3) - 2(A/A^\circ)}$$

The equilibrium constant was measured by this procedure at several acid concentrations. Optical measurements were made between 410 and 440 mμ where A/A° and $\varepsilon_4/\varepsilon_3$ are the largest, giving maximal precision in the evaluation of the equilibrium constant. The results obtained are shown in Fig. 7. The estimated probable error is shown by the vertical lines at each point.

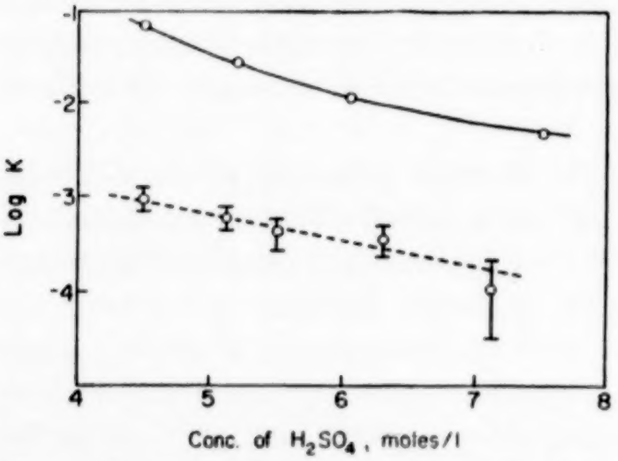

Fig. 7. Log of formal equilibrium constant for disproportionation of +3 manganese. Solid line represents values obtained by GRUBE AND HUBERICH[4], and the dotted line represents values obtained in this study.

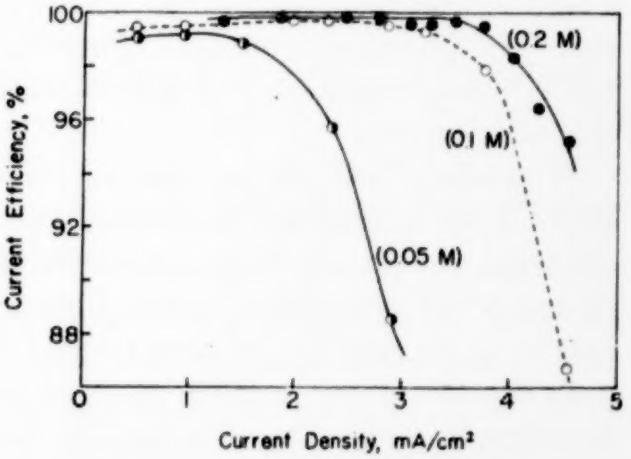

Fig. 8. Current efficiency for generation of +3 manganese in 5 M sulfuric acid as a function of current density and concentration of +2 manganese (in parentheses).

The formal equilibrium constants reported by GRUBE AND HUBERICH[5] are shown for comparison in Fig. 7. These authors evaluated the constant from e.m.f. measurements of the +2/+3 and +3/+4 couples. For the +2/+3 couple no problems are involved since constant values of the potential are rapidly obtained, which obey the Nernst expression for a one-electron oxidation–reduction couple. In solutions containing +4 manganese this is not the case. From our experience, even after 48 h there is a slow positive drift of the potential. The thermodynamic validity of potentials obtained under such conditions is questionable. The measurement of the equilibrium constant by spectrophotometry is, in our opinion, more reliable.

CURRENT EFFICIENCY FOR ELECTROGENERATION OF +3 MANGANESE

The current efficiency was determined for the generation of +3 manganese in solutions in which the concentration of +2 manganese and sulfuric acid were varied, and which were 0.025 *M* in +3 iron. A constant anodic current was passed for a measured period of time, and the +3 manganese so generated was then back-titrated by electrogeneration of ferrous iron. This procedure assumes 100% titration efficiency for the titration of +3 manganese with the electrogenerated ferrous iron. Support for this assumption lies in the fact that the cathode was maintained at a potential of about +0.5 V *vs.* N.H.E., and at this potential the contribution to the cathodic current from the reduction of hydrogen ion is known to be negligible.

A rotating platinum electrode was used to determine the end-point amperometrically in the titration of +3 manganese with +2 iron. The potential of the rotating electrode was maintained constant at +1.1 to +1.2 V *vs.* N.H.E. Sufficiently long generation times were used, so that the error in the measurement of the current efficiency is less than 0.1%.

For each solution, containing varying concentrations of +2 manganese and sulfuric acid, the current efficiency was determined over a range of anodic currents. The results shown in Fig. 8 are for solutions 5.0 *M* in sulfuric acid, in which the +2 manganese concentration was varied as indicated. The results obtained at other acid concentrations are similar. The current efficiency is not sensitive to the sulfuric acid concentration between 1 and 7 *M*, but is dependent on the +2 manganese concentration and the current density. The current efficiency decreases significantly at elevated temperatures.

The low values for the current efficiency observed at low current densities result from the fact that the over-potential for the oxidation of water (or perhaps sulfate or bisulfate) decreases with current density at a rate greater than the decrease in the overpotential for the oxidation of +2 manganese. At low current densities the contribution to the anodic current arising from reactions other than the oxidation of +2 manganese thus becomes more significant.

At high current densities the decrease in current efficiency results from the fact that the limiting current for oxidation of +2 manganese has been exceeded. However, in the oxidation of +2 manganese the limiting current is not diffusion controlled but rather is kinetically controlled. This has been confirmed by a chronopotentiometric study of this oxidation.

From this study the optimum conditions for the practical use of electrogenerated +3 manganese in coulometric titrations include a sulfuric acid concentration between about 2 and 7 *M*, a generating current density between about 1 and 4 mA/cm^2, and a relatively large concentration of +2 manganese (*e.g.*, at least 0.2 *M*). Although +3 manganese becomes less stable with increasing temperature, this does not necessarily preclude coulometric titration at an elevated temperature when the rate of the titration reaction is greater than the rate of disproportionation of +3 manganese and/or the rates of reduction of +3 and +4 manganese by water.

EXPERIMENTAL PROCEDURE

The titration cell was similar to that shown by LINGANE[6], and consisted of a 200-ml tall form, lipless beaker closed by a Teflon stopper. The auxiliary electrode consisted of a 2-cm^2 platinum foil immersed in a solution of sulfuric acid of the same concentration as in the supporting electrolyte. This solution was contained in a glass tube whose bottom was closed by a sintered glass disc, and which was immersed in the test solution. The generator electrode consisted of a round disc of perforated platinum foil with a total surface area of 10.7 cm^2. The generator electrode lay horizontally in the solution directly below the sintered glass disc at the bottom of the auxiliary electrode chamber. The solutions were continuously deaerated with nitrogen, and a magnetic stirrer provided efficient stirring.

The auxiliary electrode for the amperometric end-point detection consisted of a mercury–mercurous sulfate–6.3 M sulfuric acid electrode, in contact with the solution through a 6.3 M sulfuric acid salt bridge.

The rotating electrode consisted of a length of platinum wire, 0.5 mm in diameter, sealed in a length of soft glass tubing, with about 1 cm of the wire protruding from the end of the tube and bent in a U-shape. The glass tube was filled with mercury, providing contact between the platinum wire and the external measuring apparatus. The electrode was rotated at 780 r.p.m.

The constant current source was essentially that described by LINGANE[6].

ACKNOWLEDGEMENT

Appreciation is expressed to the National Science Foundation for a fellowship held by one of us (R.G.S.).

SUMMARY

The equilibrium constant for the disproportionation of +3 manganese into the +2 and +4 states in sulfuric acid media has been evaluated spectrophotometrically. The formal disproportionation constant varies from 10^{-3} in 4 M sulfuric acid to 10^{-4} in 7 M sulfuric acid at 25°. In 5 to 7 M sulfuric acid both +3 and +4 manganese are quite stable with respect to both their reduction by water and to the precipitation of their oxides. The current efficiency for the generation of +3 manganese is nearly 100% in 2 to 7 M sulfuric acid solution, providing the concentration of +2 manganese is at least 0.2 M. A sulfuric acid concentration of about 6 M is most satisfactory when +3 manganese is generated for coulometric titration because of the maximal stability of +3 manganese in this medium.

RÉSUMÉ

La constante d'équilibre de la dismutation du manganèse(III) en manganèse(II) et (IV) a pu être déterminée spectrophotométriquement. Une méthode est proposée pour un titrage coulométrique.

ZUSAMMENFASSUNG

Die Gleichgewichtskonstante für die Disproportionierung von Mangan(III) in Mangan(II) und Mangan(IV) konnte spektrophotometrisch ermittelt werden. Es wird eine Methode beschrieben zur coulometrischen Titration von Mangan.

REFERENCES

[1] P. TUTUNDŽIĆ AND S. MLADENOVIĆ, *Anal. Chim. Acta*, 12 (1955) 382.
[2] M. SEM, *Z. Elektrochem.*, 21 (1915) 426.
[3] A. N. CAMPBELL, *Trans. Faraday Soc.*, 22 (1926) 226.
[4] G. GRUBE AND H. HUBERICH, *Z. Elektrochem.*, 29 (1923) 8.
[5] K. VETTER AND G. MANECKE, *Z. physik. Chem.*, 195 (1950) 270, 337.
[6] J. J. LINGANE, *Electroanalytical Chemistry*, Interscience Publishers, Inc., New York 1958, pp. 496, 502.

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ELECTROSTATIC DISCHARGE METHODS OF ZONE LOCATION FOR PAPER CHROMATOGRAPHS

IV. RAPID APPROXIMATE ESTIMATIONS OF ZONE CONTENT BY STATIC DISCHARGE CURRENTS

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The writer described both rectified radio-frequency and low-frequency methods in parts I to III[1,2]. The present paper presents a simple method whereby the solute content of spots or zones may be rapidly estimated by means of condenser discharges.

The required electrical circuit is indicated in Fig. 1. R is a sensitive mirror galvanometer which is highly damped by means of a shunting resistance S. The latter is adjusted to allow a galvo deflection 'X' when the micro-conductimetric tube T is filled with distilled water. For the galvo employed the shunt required was 45 Ohms.

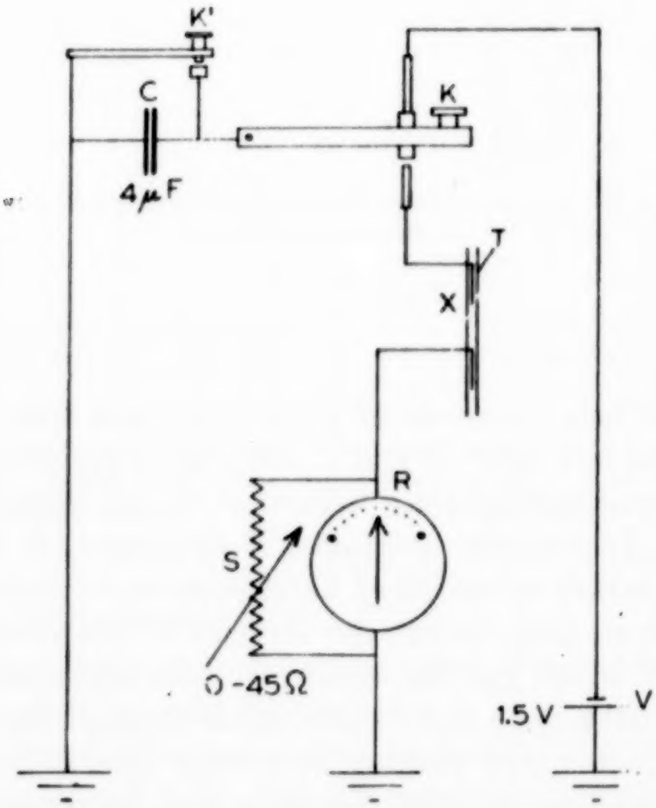

Fig. 1. Circuit diagram illustrating Blake's electrostatic discharge method for rapid zone content estimations. When a 1.5-V charging battery is employed a reflecting galvanometer is used. An ordinary micro-ammeter can take its place but in that case the charging voltage required will be higher.

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For distilled water X = 1–7 cm on the galvo scale. K and K′ are two well insulated keys of the type used for morse signalling. Key K when in the position depicted charges a 4 μF condenser C from a 1.5-V dry cell V.

X in the figure is a narrow glass tube into which samples of the liquids are drawn. The complete conductimetric tube T is illustrated in Fig. 2.

When key K′ is depressed, condenser C is discharged through the liquid content of the tube X and a galvo swing is recorded. In order to ensure that the residual charge of the condenser shall not interfere with the readings, as soon as the return swing of the galvanometer has commenced the condenser is earthed by means of key 2.

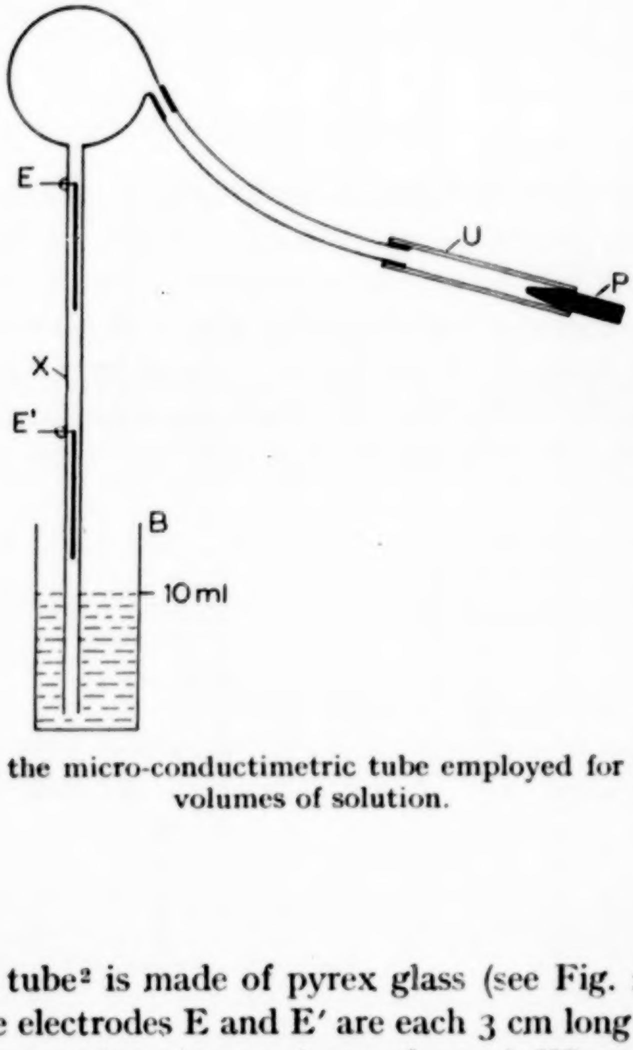

Fig. 2. This figure shows the micro-conductimetric tube employed for working with very small volumes of solution.

Conductimetric tube

The conductimetric tube[2] is made of pyrex glass (see Fig. 2). It has an internal diameter of 3 mm. The electrodes E and E′ are each 3 cm long and are separated by 3 cm. B is the solution container for a volume of 10 ml. When working with smaller volumes a proportunately smaller container is employed. A short length of rubber gas tubing as shown makes an excellent hand pressure syringe.

Instead of using an air inlet valve[3] the far end of this tube is plugged by a short length of glass rod P which can be withdrawn and replaced when it is desired to empty the conductimetric tube and to bubble air through the solution to stir it.

Before recording each galvo reading the tube should be emptied and refilled several times as the smallest amount of residue from a previous filling will affect the next measurement.

The extreme sensitivity of the apparatus provides also a most useful method for ensuring that the tube is perfectly clean before work is commenced.

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Concentration vs. galvo swing graph

Fig. 3, plotted on ordinary squared paper shows a series of dilutions of $CuCl_2$ in distilled water ranging from *N*/500 to *N*/4000 plotted against their respective galvo swings.

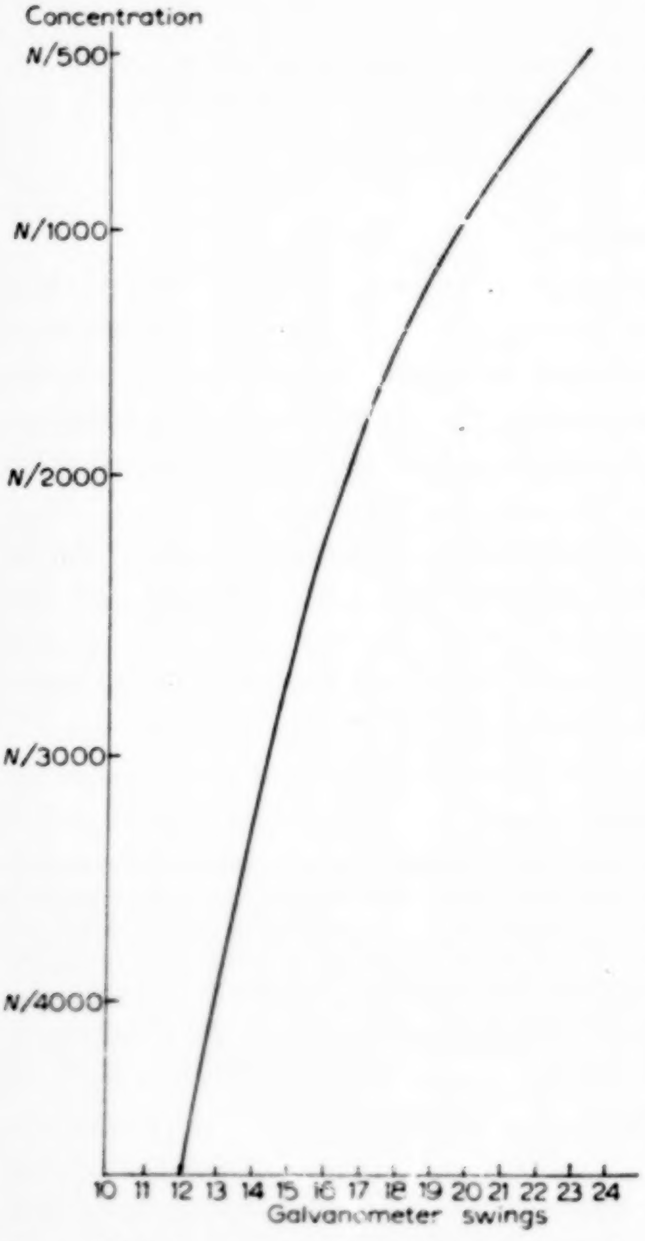

Fig. 3. This is a graph showing a series of $CuCl_2.2H_2O$ concentrations plotted against galvanometer swings on ordinary squared paper (ambient temperature 24°).

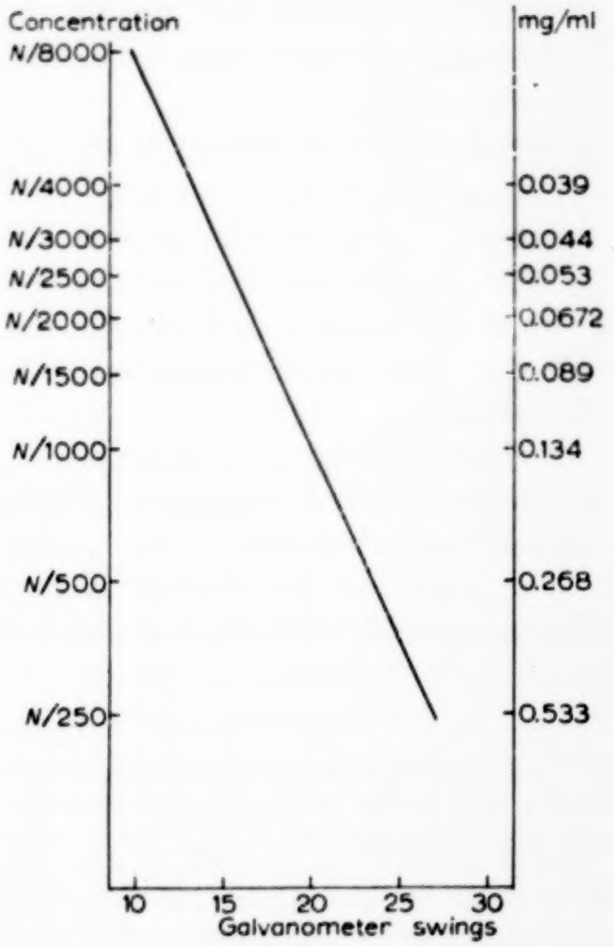

Fig. 4. This graph shows the same series of concentrations as in Fig. 3 plotted on log paper. The resultant linear graph enables both the solution concentrations and the mg content to be estimated. This chart used in conjunction with the electrostatic discharge circuit can be employed also when it is desired to make up a stock solution to any particular concentration. Spot content = mg/ml volume of solution in which it is dissolved.

Log of concentration vs. galvo swing graph

Fig. 4 shows the same series plotted on log paper. The column on the right gives the approximate milligram content of the spot or zone per cubic centimetre. To evaluate the content of a spot or zone after location it is excised and its solute is dissolved in a small measured volume X of water. Next its galvo swing is ascertained.

By reference to the log graph Fig. 4 both its concentration and its approximate mg content can be found.

Similar charts are easily prepared from $N/1$ solutions of any solute so long as the nature and molecular weight is known.

Other suggested applications

The above static discharge method provides a rapid test for the purity of water and other liquids.

For example distilled water (once distilled) gave a galvanometer swing of 1.7 on the galvo scale whilst the swing for tap water was 18.2.

No swing was observable for benzol or ether.

A simple method for dispensing in micro-quantities

Having noted how completely chromatograph spots travel away from their starting place, so completely in fact that not the slightest trace is detectable either by R.Rf. or by static discharge methods the following scheme occurred to the writer.

Firstly, a sheet of Whatman's No. 1 filter paper was soaked in a $N/1$ solution. When this was dry numerous small discs each 5 mm in diameter were punched from the paper.*

A series of these discs were added in succession to 10 ml of distilled water and a graph was plotted showing the relation 'No. of discs *vs.* galvo swings' for the various concentrations.

This graph took the form of an exceptionally even curve and showed that accurate dispensing could be carried out with such discs.

SUMMARY

This paper describs further applications of electrostatic discharge currents in paper chromatography. The swing of a mirror galvanometer due to the discharge of a condenser through various solution concentrations is employed to obtain rapid approximate determinations of the milligram content of spots and zones. The circuit is illustrated together with details of the micro-conductimetric tube. A chart is given also showing the relationship between galvo deflections and the content of any spot. It is suggested that the circuit provides a rapid method for ascertaining the purity of water, alcohol and other liquids. Finally a new method for dispensing micro quantities of any solute is described.

RÉSUMÉ

L'auteur décrit de nouvelles applications des courants de décharges électrostatiques en chromatographie sur papier. Cette technique peut être utilisée en particulier pour la détermination de la pureté de l'eau et d'autres liquides.

ZUSAMMENFASSUNG

Bei der beschriebenen Anwendung elektrostatischer Entladungsströme in der Papierchromatographie werden die Ausschläge eines Spiegelgalvanometers, die durch die Entladung eines Kondensators durch verschieden konzentrierte Lösungen hervorgerufen werden, zur Messung der Konzentration der gelösten Stoffe in den Flecken und Zonen verwendet. Anwendung zur Reinheitsbestimmung von Wasser und anderen Flüssigkeiten.

REFERENCES

[1] G. G. Blake, *Anal. Chim. Acta*, 17 (1957) 489, 492; 19 (1958) 477.
[2] G. G. Blake, *Anal. Chim. Acta*, 13 (1955) 562; 16 (1957) 240; *Electronic Eng.*, 26 (1954) 317.
[3] G. G. Blake, *Australian J. Sci.*, 14 (1951) 93.

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* An ordinary office file-punch stamps out two suitable discs at a time.

DETERMINATION OF GASES IN PLUTONIUM, URANIUM AND ZIRCONIUM BY VACUUM FUSION

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INTRODUCTION

Procedures and apparatus suitable for the routine analysis of gases in stable and radioactive metals with particular emphasis on zirconium, uranium, and plutonium were desired at the Hanford Atomic Power Operation Facilities. Due to the cost, scarcity and radioactivity of the samples, it was necessary to minimize the quantity used for analysis. That requirement was fulfilled by utilizing a sensitive method in which all the gas present in the sample is released and analyzed at one time, *i.e.*, vacuum fusion.

The metallic sample is fused with carbon in a high vacuum, and any oxygen, nitrogen, and hydrogen present are evolved[1], oxygen as carbon monoxide and nitrogen and hydrogen as elements. The method permits a simultaneous and quantitative determination of total oxygen, nitrogen, and hydrogen regardless of the form in which these elements may be present. The released gases are collected in a known volume, the total pressure measured, and the gas mixture analyzed. Although a common scheme of analysis is based on fractional freezing[2], mass spectrometric analysis was chosen here instead for several reasons: it permits detection of trace amounts of gases, nitrogen is determined directly and not by difference, and the analysis of the gas mixture can be carried out independently of the fusion apparatus.

The essential condition for successfully analyzing gases in metals by vacuum fusion techniques is that the sample be brought into intimate contact with carbon at an elevated temperature and a low pressure. These conditions are satisfied if the sample is dropped *in vacuo* into a metal bath in which an adequate amount of carbon is dissolved. In practice, because of vapor pressure, melting point, carbon solubility, and carbide formation considerations iron or platinum is used for the bath material. One of the major difficulties encountered in the iron bath technique is the great increase in viscosity of the bath with time due to its increased carbon content[3]. Within two hours, the iron melt becomes so viscous that additional samples cannot be analyzed in that particular bath. Thus the increase in viscosity seriously hampers the possibility of using vacuum fusion as a method for routine analyses. In the present work, the radioactive samples were added to the iron bath one after the other, waiting only for all the gas to be collected in a known volume and the pressure measured. The mass spectrometric analyses were performed after the melting operation was completed.

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For non-radioactive samples, a platinum bath is preferred since it does not become viscous and thus imposes no time limitations. A large platinum inventory is required because the sample-to-weight ratio should not exceed 3%. However, the platinum may be reclaimed at a nominal price so that the cost per analysis is reasonable. On the other hand, platinum used as a bath for radioactive samples must be discarded, making iron the preferred choice for radioactive samples.

The most generally accepted mechanisms explaining the quantitative release of oxygen, nitrogen, and hydrogen, respectively[4], are:

(1) Oxygen $M_xO_{y\,\mathrm{solid}} + yC_{\mathrm{solid}} \rightarrow yCO_{\mathrm{gas}} + xM_{\mathrm{liquid}}$

(2) Nitrogen $2(M_xN_y) \xrightarrow{Fe} 2\,xM_{\mathrm{in\ Fe\ solution}} + yN_{2\mathrm{gas}}$

(3) Hydrogen $2\,M_xH_y \rightarrow 2\,M_x + yH_2$

It should be noted that carbon does not enter into the second and third reactions and that the metal bath is not required for the last reaction, which is merely a thermal decomposition. When only a hydrogen determination is desired, it may be obtained by merely heating the sample in a vacuum and measuring the amount of hydrogen liberated, a procedure known as vacuum extraction[5].

EXPERIMENTAL

Apparatus

The vacuum system designed for the present work may be divided into three main sections: a furnace assembly in which gases are evolved by heating or fusing the samples, a gas collecting system where the evolved gases are pumped into a known

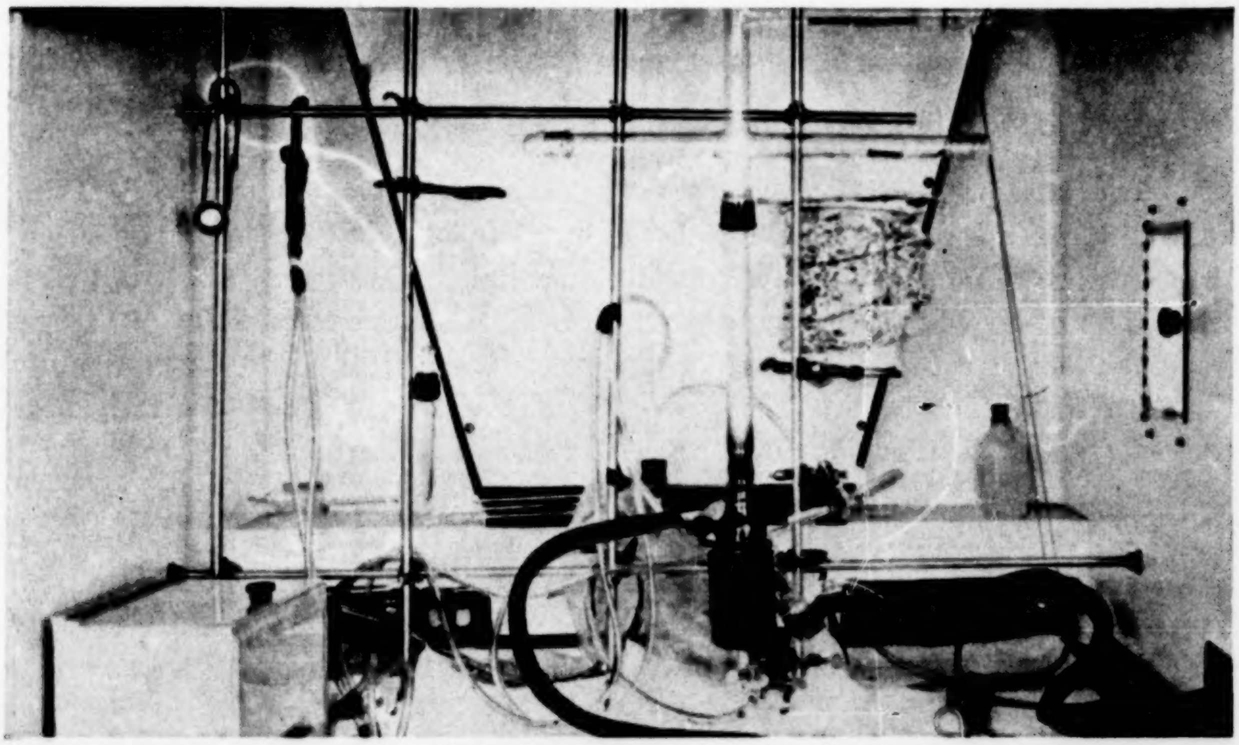

Fig. 1. Furnace assembly.

volume and their pressure measured, and a sampling manifold where the gases are transferred into bulbs which are taken to a mass spectrometer for analysis.

The furnace assembly is shown in Fig. 1. The furnace tube is made entirely of quartz and consists of a ground joint connected to 26 mm tubing which in turn is connected to a section of 52 mm tubing with the lower end rounded off to form the bottom. For vacuum fusion work, a graphite crucible surrounded by lampblack is placed in the furnace tube. The crucible is heated inductively and crucible temperatures of 2400° are obtainable while the furnace tube does not heat above 500°.

The quartz tube is sealed to a loading tree consisting of a vertical glass tube onto which are connected four horizontal arms. One arm is used to connect the tree to the rest of the vacuum system and the other arms are used to hold the samples and the pieces of hydrogen-fired iron used for the bath. At the upper end of the tree is a ground joint to which a cap containing an optical window is sealed. The temperature of the graphite crucible is measured with an optical pyrometer by sighting through the optical window which was constructed by sealing one end of a Beckman spectrophotometer cell to a ground joint. The loading tree and furnace tube are enclosed in a hood which is converted to a glove box during plutonium work.

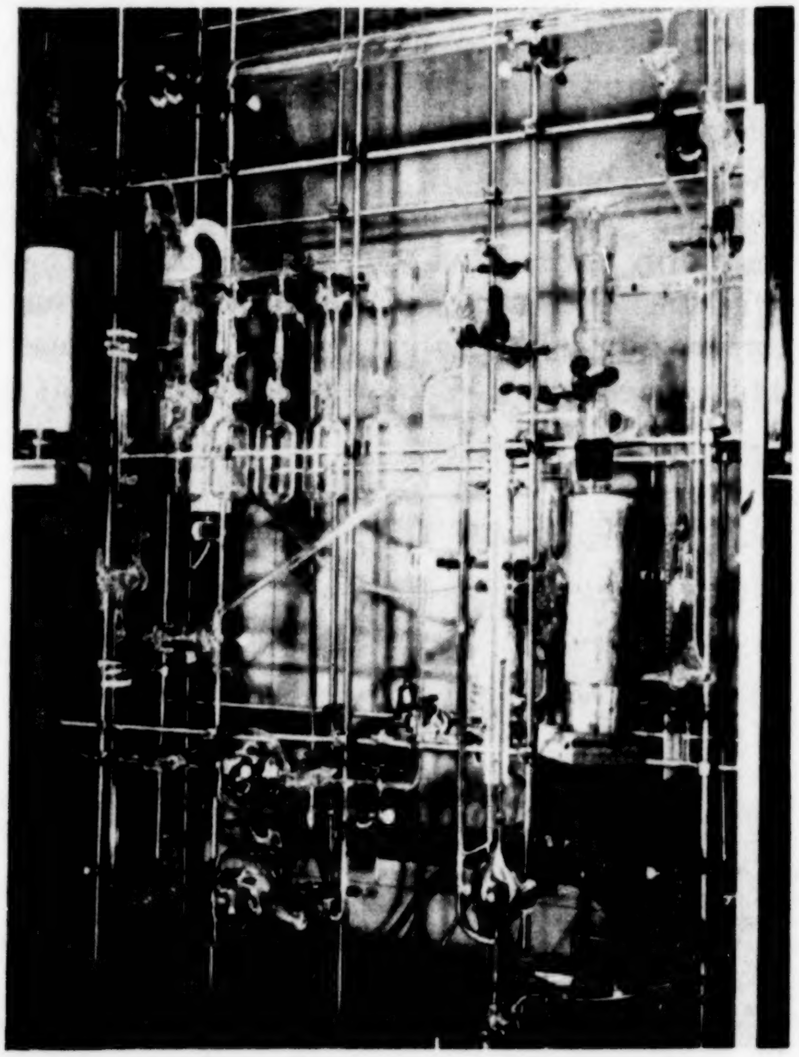

Fig. 2. Gas collecting and analyzing system.

An all glass high vacuum system shown in Fig. 2 is used for the gas collecting system. Gases evolved from the furnace tube are pumped by a mercury diffusion pump into one several possible combinations of calibrated volumes where the pressure is measured by use of a McLEOD gauge. The gas is then pumped by the same mercury diffusion pump from the calibrated volumes into a sampling manifold where five sample bulbs are attached by means of standard ground joints. There is a stopcock on each bulb and one above each joint. The volume of the manifold is small in comparison to the volume of a sample bulb so the majority of the gas is collected in a bulb. The sampling bulbs are used to transfer the gas mixtures to a mass spectrometer for analyses.

Procedure

Cleaned and weighed samples are placed in one side arm of the loading tree and hydrogen-fired iron pellets are placed in a second arm. The system is evacuated and the graphite crucible outgassed at 2100° until a low rate of gas evolution is attained. The iron pellets are added to the crucible, outgassed below their melting point and then melted. The blank rate at 1900° is determined. A sample is added to the melt and the released gases collected until the blank rate is re-established. The majority of the gas is transferred to a sample bulb and the remainder is pumped out. The temperature is momentarily lowered to about 1100° while a piece of vacuum-melted tin is dropped into the crucible. The tin immediately volatilizes from the crucible and condenses on the furnace tube walls, coating them with a thin layer which covers up any reactive metal film which may have formed and thus prevents gettering of gases.

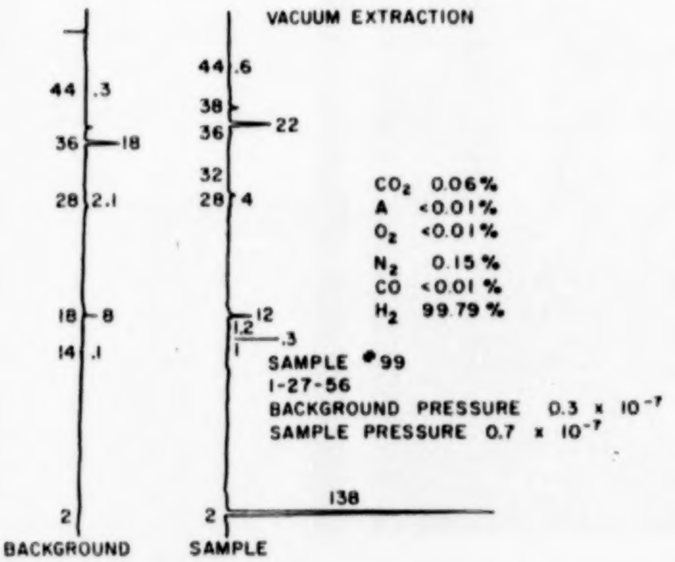

Fig. 3. Mass spectrum of gases released by vacuum extraction.

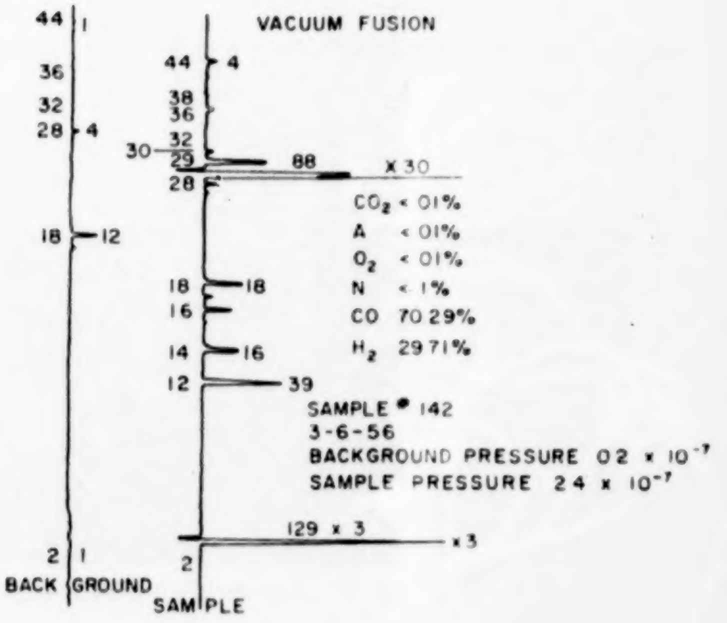

Fig. 4. Mass spectrum of gases released by vacuum fusion.

The next sample is added to the melt and the procedure is repeated until all samples have been added. The gas mixtures contained in the bulbs are taken to a mass spectrometer for analyses. From the measured pressures in known volumes, mass spectrometer results, and sample weights, the results are calculated.

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The only precautions taken during work with plutonium are to convert the hood to a glove box and to use a separate furnace tube and loading tree. Only minor amounts of contamination have been spread outside the glassware, permitting the glove box to be reconverted to a hood following a plutonium run.

Results

Typical mass spectra obtained by vacuum extraction and vacuum fusion are shown in Figs. 3 and 4, respectively. The mass spectrum shown in Fig. 3, which was obtained for the gases released from a zirconium sample heated at 1300°, demonstrates that only hydrogen is evolved by this procedure. The mass spectrum obtained by vacuum fusion of a duplicate sample (Fig. 4) contains, in addition to the hydrogen contribution, peaks at masses 28, 16, 14, and 12 due to carbon monoxide and nitrogen. These two gases are quantitatively differentiated by standard techniques using the cracking patterns of the pure gases.

Oxygen, hydrogen and nitrogen values obtained using a platinum bath were compared to these obtained with an iron bath. Plutonium samples with a gas content of 150 p.p.m. oxygen, 90 p.p.m. N_2, and 60 p.p.m. H_2 were chosen for the experiment. The results agreed within 10, 6, and 3 p.p.m., respectively demonstrating that either metal may be employed.

TABLE I

RESULTS IN P.P.M. OF HYDROGEN ANALYSES OF ZIRCONIUM SAMPLES

Sample number	*Calculated value*	*Hanford vacuum extraction*	*Hanford vacuum fusion*	*Battelle vacuum extraction*
1	46.3	46 48		48
2	50.8	55 51		56
3	112	116 110		114
4		16	15 18	
5		39	45	
6		20	21 15 15	
7		18	14 23	
8	99.9	100	94	

The results of hydrogen analyses on zirconium samples are given in Table I. Samples 1 through 3 show the typical agreement obtained by vacuum extraction procedures while samples 4 through 8 compare hydrogen values obtained by vacuum extraction and vacuum fusion. Vacuum fusion yields the poorer results as is to be expected from the fact that hydrogen constitutes only a fraction of the total gas evolved during the fusion procedure.

The results of oxygen analyses of zirconium samples are presented in Table II. Samples 1 through 3 were obtained from the Bureau of Mines and the results are in excellent agreement with their values. Samples 4 through 8 were picked at random from a group of samples analyzed by the chlorine residue method and vacuum fusion. Good agreement was obtained in some cases. However, in others the results differ significantly. High vacuum fusion results are unlikely since the pressure rise is measured until the blank rate is regained, although low values result from incomplete reaction or readsorption of the gases. Therefore, in those instances where the fusion result is the higher, it is believed to be the more accurate. Zirconium nitride, which is more stable than zirconium oxide, was not successfully determined by vacuum fusion. All gases in plutonium and uranium are readily evolved as are the oxygen and hydrogen from zirconium.

TABLE II

RESULTS IN P.P.M. OF OYYGEN ANALYSES OF ZIRCONIUM SAMPLES

Sample number	*O_2 standard*	*Vacuum fusion*	*Residue method*
1	1000	970, 980, 970	
2	1050	1040	
3	1100	1090, 1070	
4		920	930
5		980	990
6		930	990
7		1030	830
8		1060	750

In general, vacuum fusion techniques are reproducible and consistent with results obtained with other acceptable methods. The apparatus and techniques described provide a method whereby the gases present in five separate metallic samples may be collected in one melting operation of less than two hours duration.

ACKNOWLEDGEMENT

The author is indebted to E. P. GALBRAITH, E. W. CHRISTOPHERSON and G. J. ALKINE for their assistance in this work.

SUMMARY

A vacuum fusion system suitable for routine analysis of gases present in plutonium, uranium, and zirconium was built and acceptable results were obtained with the exception of the determination of nitrogen in zirconium. Hydrogen is evolved by heating the metal in a vacuum while all gases are released by fusing the sample at 1900° in a metal bath contained in a graphite crucible. The gases evolved from each sample are collected in individual bulbs for later mass spectrometric analyses. Hydrogen values within 5% and oxygen values within 10% are obtained on zirconium standards. The results for plutonium samples analyzed by the iron and platinum bath techniques are in satisfactory agreement. The apparatus and techniques described provide a method whereby the gases present in 5 separate metallic samples may be collected in one melting operation of less than two hours duration.

RÉSUMÉ

Un appareillage est proposé pour l'analyse en série des gaz présents dans des métaux stables et radioactifs, en particulier dans le plutonium, l'uranium et le zirconium. On procède par fusion au vide; les gaz recueillis sont ensuite analysés au spectromètre de masse. Des résultats satisfaisants ont été obtenus sauf pour le dosage de l'azote dans le zirconium.

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ZUSAMMENFASSUNG

Es wird eine Apparatur beschrieben zur serienmässigen Bestimmung der Gase in Plutonium, Uran und Zirkonium nach dem Vakuum-Schmelz-Verfahren. Die Analyse des extrahierten Gasgemisches erfolgt mit dem Massenspektrographen. Das Verfahren versagt bei der Bestimmung des Stickstoffes in Zirkonium.

REFERENCES

[1] R. S. McDonald, J. E. Fagel and E. W. Balis, *Anal. Chem.*, 27 (1955) 1632.

[2] J. N. Gregory and D. Mappr, United Kingdom Atomic Energy Research Establishment, *Report AERE-C-R-1274*, (1953).

[3] W. H. Smith, *Anal. Chem.*, 27 (1955) 1636.

[4] H. A. Sloman and C. A. Harvey, *J. Inst. Metals*, 80 (1951) 391.

[5] R. K. McGeary, U. S. Atomic Energy Comm., *Report WAPD*, (1952) 61.

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THE DETERMINATION OF AMINOPHENOLS AND AMINOBENZOIC ACIDS

A STUDY OF EXTRACTION PROCEDURES APPLICABLE TO BIOLOGICAL MATERIALS

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Although sensitive colorimetric procedures exist for the determination of aminophenols and aminobenzoic acids, their direct application to biological materials, *e.g.* urine is beset with difficulties and most usually when concentrations are low. Preliminary extraction appears to be a necessity, not only as an aid to concentration but to eliminate interfering substances, *e.g.* phenols, hydroxy-aromatic acids. The use of solvent extraction and ion-exchange resins have been studied for this purpose.

In this communication, investigations have been limited to *o*- and *p*-aminophenols, *o*- and *p*-aminobenzoic acids and 3-hydroxyanthranilic acid. Examples of typical results are shown.

EXPERIMENTAL

Analysis of extract

The following colorimetric methods were employed to assess the quantity of substance under investigation in the various extracts.

o- and *p*-aminobenzoic acids, diazotisation with nitrous acid followed by coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride[1,2].

p-Aminophenol, indophenol pigment formation in the presence of *o*-cresol and ammonia[3,4] or molybdenum blue formation[5].

3-Hydroxyanthranilic acid, indophenol pigment formation in the presence of 2,6-dichloroquinone chlorimide[4] or molybdenum blue formation[5].

o-aminophenol, indophenol pigment formation in the presence of 2,6-dichloroquinone chlorimide[4] or molybdenum blue formation[5].

Solvent extraction

As a preliminary, the mixture rendered normal with respect to hydrochloric acid, was extracted 4 times with ether, with the intent of removing interfering substances such as phenols and hydroxy-aromatic acids. It was hoped that this process would only remove minimal quantities of the substances under investigation.

From the residual aqueous mixture, 3-hydroxyanthranilic acid and the amino-benzoic acids were extracted by ether at pH 3.0 and the aminophenols by ether at pH 7.0[1].

The substance contained in 10 ml of *N* hydrochloric acid was extracted 4 times with 40-ml quantities of ether. The extractions were carried out in 50-ml glass stoppered measuring cylinders. The mixtures were shaken vigorously for 2 min and after separation, the ether extracts were separated with a teat pipette.

Amino-benzoic acids/3-hydroxyanthranilic acid

The pH of the residual aqueous fluid was adjusted to 3.0 by the addition of saturated sodium acetate solution. The solution was then extracted 3 times with 40-ml quantities of ether as described above.

TABLE I

The recovery of *o*- and *p*-aminobenzoic acids by ether extraction (A) from *N* HCl at pH 3.0

	Quantity taken μg	*From N HCl*		*At pH 3.0*	
		Quantity recovered μg	*% recovered*	*Quantity recovered μg*	*% recovered*
o-Aminobenzoic acid					
	20	5.5	27.5	3.2	16.0
	40	10.8	27.0	6.0	15.0
	80	21.7	27.1	13.0	16.2
p-Aminobenzoic acid					
	20	1.6	8.0	10.0	50.0
	40	3.2	8.0	19.2	49.0
	80	6.2	7.7	42.5	53.1

The recovery of 3-hydroxyanthranilic acid, *o*- and *p*-aminophenol, by ether extraction at pH 3.0

	Quantity taken μg	*Quantity recovered μg*	*% recovered*
3-Hydroxyanthranilic acid			
	10	6	60
	20	11	55
	50	27	54
	100	56	56
o-Aminophenol (pH 7.0)			
	12.5	11	88
	25	21	84
	50	43	86
	100	88	88
p-Aminophenol (pH 7.0)			
	12.5	11	88
	25	21	84
	50	46	92
	100	91	91

Note: The extractions at pH 3.0 and 7.0 followed on those from *N* HCl.

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Aminophenols

The pH of the residual aqueous fluid was adjusted to 7.0 by the addition of solid sodium bicarbonate. The solution was then extracted 3 times with 40-ml quantities of ether as described above.

Ether extracts were evaporated to dryness in an all glass vacuum still.

Typical results are shown in Table I.

Although 3-hydroxyanthranilic acid is not extracted from aqueous solution by ether at pH 7.0, the aminophenols are partially extracted by ether from aqueous solution at pH 3.0. Extracts containing 3-hydroxyanthranilic acid may therefore be contaminated with aminophenols if such are present in the aqueous phase. Interference tends to occur in the determination of 3-hydroxyanthranilic acid when aminophenols are present.

The following differential solvent extraction procedure appears to be satisfactory and may be applied to an extract obtained from an ion-exchange resin.

The pH of 1 ml of an aqueous solution, normal with respect to hydrochloric acid, was adjusted to 7 by the addition of 8% sodium bicarbonate solution. The solution was extracted 3 times with 40-ml quantities of ether. These combined ether extracts may be used for the determination of aminophenols. 1 ml of 10 *N* hydrochloric acid was added to the aqueous residue, the pH of which was then adjusted to 3 by the

TABLE II

The recovery of *o*- and *p*-aminophenols and 3-hydroxy-anthranilic acid by ether extraction

	Quantity taken µg	*Quantity recovered* µg	*% recovered*
o-Aminophenol (pH 7)			
	25	23	92
	50	48	96
	100	93	93
p-Aminophenol (pH 7)			
	25	22	88
	50	47	94
	100	94	94
3-Hydroxyanthranilic acid (pH 3.0), following extraction at pH 7.0			
A.	50	43	86
	100	87	87
	200	192	96
B. in the presence of 200 µg *o*-aminophenol			
	50	42	87
	100	92	92
	200	190	95
C. in the presence of 200 µg *p*-aminophenol			
	50	43	86
	100	92	92
	200	194	97

addition of a saturated solution of sodium acetate. This solution was extracted 3 times with 40-ml quantities of ether. These combined ether extracts were then used for the determination of 3-hydroxyanthranilic acid, after evaporation to dryness.

Some typical results are shown in Table II.

ION-EXCHANGE RESINS

Examinations were limited to the use of the ion-exchange resin Dowex 50 (H^+). The technique employed was very similar to that used by BROWN AND PRICE[6] in an examination of metabolites of tryptophan in urine.

Preparation of the column

The resin (200–400 mesh) was contained in a glass tube fitted with a sintered glass base (Quickfit and Quartz Ltd.). The dimensions of the operational column were: height/70 mm; diameter/10 mm. Flow rate was controlled at 30 ml/h.

Before use the column was washed with 80 ml of 8 *N* hydrochloric acid followed by 200 ml of water. Immediately before use, the column was washed with 25 ml of 0.1 *N* hydrochloric acid.

Operation of the column

The substance under examination was applied to the column in 100 ml of 0.1 *N* hydrochloric acid. Elutions were carried out with 80 ml of 0.5 *N*, *N*, 2.5 *N* and 5 *N* hydrochloric acid respectively. All fluids that had passed through the column were collected and evaporated to dryness in an all glass still. The residues were dissolved in 10 ml of water.

Some typical results are shown in Table III.

TABLE III

THE ELUTION BY HYDROCHLORIC ACID OF *o*- AND *p*-AMINOBENZOIC ACIDS, 3-HYDROXYANTHRANILIC ACID, *o*- AND *p*-AMINOPHENOLS

The figures refer to the % of the original quantity determined in the respective eluate

Quantity in µg	*Concentration of hydrochloric acid*				
	0.1 N	*0.5 N*	*N*	*2.5 N*	*5 N*
o-Aminobenzoic acid					
1000	—	—	1.5	99.5	0.5
500	—	—	0.6	90.0	9.5
250	—	—	1.5	97.0	2.0
150	—	—	2.3	93.0	5.7
p-Aminobenzoic acid					
1000	—	—	1.3	78.0	22.0
500	—	—	1.6	85.0	15.0
200	—	—	0.8	64.7	37.5
100	—	—	5.3	87.1	9.6
3-Hydroxyanthranilic acid					
1000	—	0.8	35.0	50.5	2.8
500	—	0.6	16.3	75.4	1.2
250	—	0.1	36.3	64.6	0.3
o-Aminophenol					
1000	—	1.9	48.3	41.6	6.4
500	—	2.6	50.4	39.4	7.6
250	—	3.2	52.6	38.6	3.6
p-Aminophenol					
1000	—	2.1	31.6	66.2	3.2
500	—	1.9	29.2	64.6	4.4
250	—	1.7	32.9	60.2	3.8

RESULTS AND DISCUSSION

Determinations of many substances in biological materials must be preceded by a preliminary separation in order to increase concentration or to eliminate interfering substances. More than one stage may be necessary especially if there is interference from substances mutually separated.

The aminophenols appear to be separated equally efficiently by ion-exchange resin or by solvent extraction at pH 7. When solvent extraction at pH 7 is preceded by ether extraction at pH < 1, slight losses are encountered but these are proportional within the range examined. Such losses may be countered by submitting standards to the same treatment or by the use of a pre-determined correction factor. Examination of eluates from ion-exchange columns requires the use of the combined *N* and 2.5 *N* HCl extracts. The percentage found in the other extracts is low and such may be countered by the use of standards submitted to the same treatment or by the use of a pre-determined correction factor. Eluates from columns would contain 3-hydroxyanthranilic acid if present. Such may be eliminated by using the solvent extraction technique at pH 7.

Separation of 3-hydroxyanthranilic acid by ether at pH 3.0 following on ether extraction at pH < 1 does result in losses. Within the range examined these losses appear to be proportional hence an appropriate correction factor may be employed. Separation of 3-hydroxyanthranilic acid by ion-exchange resins (*N* and 2.5 *N* hydrochloric acid eluates) results in negligable losses. The latter would appear to be the preferable procedure. Separation of 3-hydroxyanthranilic acid from aminophenols would appear to be a quantitative procedure and probably most generally applicable to eluates from ion-exchange columns.

Separation of aminobenzoic acids from biological fluids by solvent extracted is best effected at pH 3 following ether extraction at pH < 1 to remove interfering substances. This procedure involves losses which are much higher in the case of the *ortho* compound. Percentage recoveries at pH 3 are linear over the range examined in the case of both compounds. Standards prepared under similar conditions are a necessity. Separation of the aminobenzoic acids by ion-exchange resins (2.5 *N* and 5 *N* hydrochloric acid eluates) results in negligable losses. The latter would appear to be the preferable procedure.

The procedures described have been found to be applicable to biological fluids, *e.g.* urine.

In the present investigation, the use of ion-exchange resins has been limited to the use of a fixed volume of eluting agent and also a limited number of eluates. The range of such could no doubt be greatly extended.

SUMMARY

Extraction procedures (solvent and ion-exchange resin) have been studied with regard to their potential use in the determination of aminophenols, aminobenzoic acids and 3-hydroxyanthranilic acid in biological materials.

RÉSUMÉ

Des procédés d'extraction (par solvant et par résine d'échange d'ions) ont été examinés en vue d'une application des dosages d'aminophénols, d'acides aminobenzoïques et de l'acide hydroxy-3-anthranilique dans des substances biologiques.

ZUSAMMENFASSUNG

Es wird die Anwendungsmöglichkeit von Extraktionsverfahren (Lösungsmittel und Jonen-

austauscherharze) bei der Bestimmung von Aminophenolen, Aminobenzoesäuren und 3-Hydroxyanthranilsäure in biologischen Substanzen untersucht.

REFERENCES

1 S. L. Tompsett, *Clin. Chim. Acta*, 4 (1959) 411.
2 A. C. Bratton and E. K. Marshall, Jr., *J. Biol. Chem.*, 128 (1939) 537.
3 D. J. Lawford and D. G. Harvey, *Analyst*, 78 (1953) 63.
4 S. L. Tompsett, *Clin. Chim. Acta*, 3 (1958) 149.
5 A. P. Briggs, *J. Biol. Chem.*, 51 (1922) 451.
6 R. R. Brown and J. M. Price, *J. Biol. Chem.*, 219 (1956) 981.

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DETERMINATION OF FREE ACID IN URANIUM(VI) SOLUTIONS BY MEANS OF CATION EXCHANGERS

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INTRODUCTION

The usual titration with a standard base cannot be used for the determination of free acid in uranium(VI) solutions, owing to hydrolysis effects. In early methods this interference was prevented by precipitating uranium as peroxide or ferrocyanide and its subsequent removal by filtration[1]. It can also be eliminated by adding a complexing agent, *e.g.* oxalate[2] or fluoride[3-7], which inactivates the uranyl ion. The effect of some other hydrolyzable ions, *e.g.* aluminium[8] or thorium[9] can be eliminated in the same way. The neutralization point in the subsequent titration can be determined visually, potentiometrically[6] or conductometrically[2,5]. Another possibility for the determination of the free acid can be based on the fact that the pH value of a nearly neutral uranyl nitrate solution is a sensitive indication of its free acid content. The acid should first be neutralized by a standard alkali so that its concentration does not exceed 0.1 N. After determining the pH, the acid content can be found from curves for known uranyl nitrate concentrations. To obtain the free acid, this content is to be corrected for the neutralized acid[10,11].

In this paper an ion-exchange method for free acid determination is described. It requires very little solution, and is suitable for wide range of uranium and free acid concentrations. The solutions are passed through a column of the cation exchanger in the hydrogen form. To determine the free acid, it is necessary to titrate the total acid in the effluent and to subtract the amount equivalent to uranium. The amount of uranium is determined on a separate sample.

It should be noted that Samuelson[12] used same principle to determine the total amount of ions in salt solutions, and Bhatnagar[13] to estimate the free nitric acid in uranyl nitrate.

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EXPERIMENTAL

Apparatus and reagents

Unicam Spectrophotometer SP 500, glass cells 1 cm. Magnetic stirrer with polythene-covered stirring bar. Ion-exchange column: 2 g of air-dried Dowex 50, 8% cross-linked, H-form, 100–150 mesh; capacity 3.6 mequivs./g; column dimensions 100 mm high, 8 mm diameter.

Uranyl nitrate hexahydrate, B.D.H., Lab. reagent. Uranyl sulphate obtained from the nitrate by metathesis on Dowex 50.

Distilled water, freshly prepared, and showing no traces of acidity when filtered through the hydrogen-saturated ion exchanger[12].

Procedure

Pass a sample of the solution through the column of Dowex 50 resin in the hydrogen form at a flow rate of approximately 1 ml/min into a 50-ml Erlenmeyer flask. Wash the column with water until neutral and titrate the combined effluent and wash-water with standard 0.1 *N* sodium hydroxide against methylorange. Separately determine the uranium content of the solution. Subtract the quantity of acid equivalent to uranium from that obtained by titration. The column is easily regenerated with 6 *N* hydrochloric acid, and after washing with water until neutral, can be used again.

Note: If, for any reason, it is not desirable to determine uranium in the original solution, the uranium can be eluted from the column.

RESULTS

The procedure was tested with nitric acid solutions of uranyl nitrate. In these solutions the uranium/free acid ratio (in equivs.) was varied from 1:25 to 52:1, and the acid concentrations from 0.02 to 7.6 *N*. Uranium was determined spectrophotometrically by the thioglycolate method[14]. Some results are presented in Table I.

TABLE I

DETERMINATION OF FREE NITRIC ACID IN SOLUTIONS OF URANYL NITRATE

	Taken		*Mequivs. U*	*Found mequivs.* HNO_3	*Error %*
Sample, ml	*Mequivs. U*	*Mequivs.* HNO_3	*mequivs.* HNO_3		
1.00	0.830	0.016	52:1	0.019	+18.75
0.50	0.247	0.025	10:1	0.024	— 4.00
0.50	0.255	0.051	5:1	0.050	— 1.96
2.00	0.503	0.148	3.4:1	0.146	— 1.35
0.50	0.086	0.429	1:5	0.421	— 1.86
0.50	0.228	2.285	1:10	2.313	+ 1.22
0.50	0.152	3.796	1:25	3.779	— 0.45
2.00	2.991	4.273	1:1.4	4.282	+ 0.21
1.00	0.457	4.570	1:10	4.587	+ 0.37
2.00	2.991	8.200	1:2.8	incomplete adsorption	

When the quantity of uranium equals half the resin capacity, it is possible to use 2 ml of the 2.5 *N* nitric acid solution. At a greater acid concentration, the adsorption of uranium is incomplete. The uranium/free acid ratio has only a slight effect on the results. For instance, at a ratio of 1:20, the maximum deviation is ± 2.0%, and at 10:1, with the same acid concentration, the deviation is ± 2.3%.

To find out the minimum quantity of acid which can be determined with reasonable accuracy, solutions with various acid concentrations were analyzed. In the most unfavourable case, *viz.* an aliquot of 0.0080 mequivs. of acid (100 λ) with a uranium/free acid ratio of 7:1 and a free acid concentration of 0.080 N, the value of 0.0081 ± 0.0005 mequivs. was found (101 ± 6.3%). For these investigations smaller columns containing approximately 0.5 g of resin were used (resin beds 50 × 5 mm).

The proposed procedure can also be used for solutions of hydrolyzable cations other than uranium. The solutions may contain more than one hydrolyzable cation, if these can be determined simply and with a sufficient accuracy. In Table II free acid contents are given for solutions containing both uranium and aluminium. Uranium and aluminium were determined spectrophotometrically in original solutions: uranium as above, and aluminium with aluminon in acid medium[15]. The direct determination was possible as both methods are insensitive to foreign cations. At greater uranium concentrations, aluminium can be determined by the same method, but in alkaline medium[7].

TABLE II

DETERMINATION OF FREE NITRIC ACID IN SOLUTIONS OF URANYL NITRATE AND ALUMINIUM NITRATE

Taken (mequivs.)			*Found nitric acid mequivs.*	*Error %*
Uranium	*Aluminium*	*Nitric acid*		
0.140	0.405	2.068	2.093	+1.21
0.132	0.448	2.098	2.076	−1.05
0.355	0.448	2.098	2.106	+0.38

The same procedure can be used to determine free sulphuric acid in uranyl sulphate solutions (Table III). Columns with resin beds of 50 × 5 mm were used. Uranyl ion has a greater tendency to form negatively charged complexes in sulphuric acid than in nitric acid medium, which restricts the use of concentrated sulphuric acid solutions. It is, however, always possible to dilute the solution to the acidity at which the adsorption of uranium is quantitative.

TABLE III

DETERMINATION OF FREE SULPHURIC ACID IN SOLUTIONS OF URANYL SULPHATE

Taken			*Mequivs. U*	*Found mequivs.* H_2SO_4	*Error %*
Sample, ml	*Mequivs. U*	*Mequivs.* H_2SO_4	*Mequivs.* H_2SO_4		
1.00	0.246	0.340	1: 1.4	0.340	±0.00
1.00	0.246	1.263	1: 5.1	1.264	+0.05
1.00	0.246	2.836	1:11.5	incomplete adsorption	
2.00	0.246	2.836	1:11.5	2.822	−0.49

SUMMARY

An ion-exchange method for the determination of free acid in solutions containing uranium(VI) is described. The solution is passed through a cation exchanger in the hydrogen form and the total acidity is determined as well as the uranium content of the original solution; the free acid is then calculated. The method is also applicable to solutions containing other hydrolyzable cations.

RÉSUMÉ

Une méthode par échange d'ions est proposée pour le dosage de l'acide libre dans des solutions d'uranium(VI). Elle peut être également appliquée à d'autres solutions de cations hydrolysables.

ZUSAMMENFASSUNG

Freie Säure in Uran(VI) Lösungen kann nach Behandlung der Lösung mit einem Kationenaustauscher in der H-Form durch Titration des Eluates bestimmt werden. Anwendungsmöglichkeiten für andere hydrolysierbare Verbindungen werden erwähnt.

REFERENCES

[1] C. J. RODDEN, *Analytical Chemistry of the Manhattan Project*, McGraw-Hill Book Co., Inc., New York 1950, pp. 214–216.

[2] G. L. BOOMAN, M. C. ELLIOT, R. B. KIMBALL, F. O. CARTAN AND J. E. REIN, *Anal. Chem.*, 30 (1958) 284.

[3] ROBERT LEE MOORE AND A. R. SCHMIDT, *HW-14603* (1957).

[4] L. P. PEPKOWITZ, W. W. SABOL AND D. DUTINA, *Anal. Chem.*, 24 (1952) 1956.

[5] R. C. PROPST, *DP-76* (1955).

[6] O. MENIS, D. L. MANNING AND G. GOLDSTEIN, *ORNL-2178* (1956).

[7] M. J. SHEPHERD, JR. AND J. E. REIN, *Manual of the Analytical Methods Used by the Control Laboratory at the Chemical Processing Plant*, IDO-14316 (1955).

[8] T. EDER. *Z. anal. Chem.*, 119 (1940) 399.

[9] W. W. SABOL AND B. F. RIDER, *KAPL-1477* (1956).

[10] G. J. ALKIRE, *Anal. Chem.*, 24 (1952) 1228.

[11] M. E. JAMES, B. F. RIDER AND H. C. HENDRICKSON, *KAPL-1497* (1956).

[12] O. SAMUELSON, *Ion Exchangers in Analytical Chemistry*, J. Wiley & Sons, New York 1953, p. 117.

[13] D. V. BHATNAGAR, *J. Sci. Ind. Research*, 16B (1957) 23.

[14] W. H. DAVENPORT, JR. AND P. F. THOMASON, *Anal. Chem.*, 21 (1949) 1093.

[15] C. J. RODDEN, *Analytical Chemistry of the Manhattan Project*, McGraw-Hill Book Co., Inc., New York 1950, p. 388.

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RESORCINOL AS A REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF FERRIC IRON

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In a recent communication the use of resorcinol as a reagent for the spectrophotometric determination of uranium has been reported[1]. Resorcinol gives a violet colour with ferric ions, which is unaffected by ferrous ions. In contrast to existing methods[2-5] the preparation of the reagent is simple. The use of resorcinol as a reagent for the spectrophotometric determination of ferric iron is described in this paper.

EXPERIMENTAL

Absorption measurements were made on Coleman's Universal Spectrophotometer, Model 14. A Marconi pH meter was employed for pH measurements. A freshly prepared solution of resorcinol (Merck's pure quality) was used for the measurements. Solutions of ferric chloride (AnalaR) were freshly prepared and the iron content was determined gravimetrically as Fe_2O_3. Suitable AnalaR salts were used for testing the interference of cations and anions.

DISCUSSION

The absorption spectra of the coloured species (0.004 M ferric chloride and 0.4 M resorcinol, Curve A, and 0.008 M ferric chloride and 0.08 M resorcinol, Curve B, in aqueous media) in presence of excess of resorcinol is shown in Fig. 1 along with that of the pure reagent of the same concentration, Curve C. The coloured product has an appreciable absorption at 450 mμ while the reagent has negligible absorption. The wavelength mμ was selected to study the various factors described below.

Colour intensity and pH

The pH of the solution has a considerable effect on the colour intensity. Solutions containing the same amounts of ferric chloride and resorcinol (in excess) were prepared at different pH values and their absorption was measured. The results (Fig. 2) indicate that the colour intensity reaches a maximum at pH 2.9. Excess of reagent, even more than a ten-fold excess, has no influence on the colour intensity.

Stability of the colour and the sensitivity of the reagent

The solution attains its maximum intensity immediately after the addition of reagent. The colour is stable for about five hours at room temperature and then fades slowly. The reagent solution is initially slightly brown and slowly darkens on standing for several days. On heating, the colour decreases appreciably and disappears completely at about 75°. The corrected optical densities of solutions containing 0.5, 0.8, 1.0 and 2.0 p.p.m. of ferric chloride showed that the smallest amount of ferric ion that can be detected is 1.0 p.p.m.

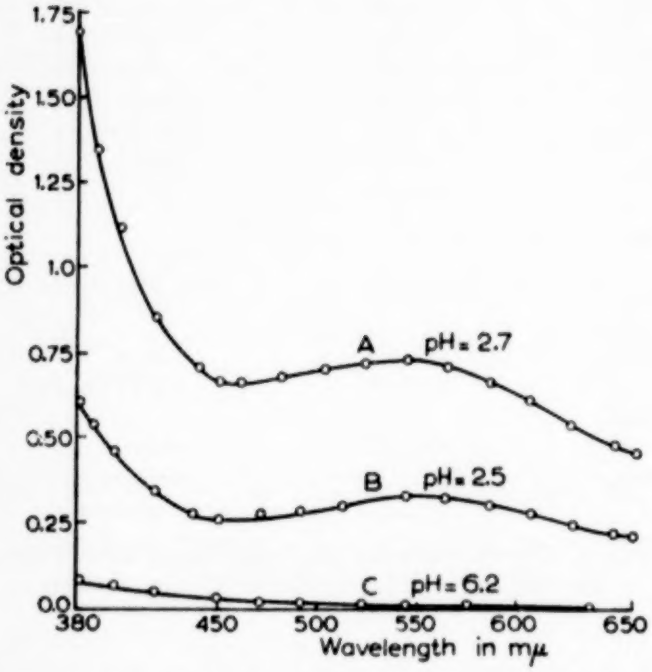

Fig. 1. Curve C: absorption of an aqueous solution of resorcinol (0.04 *M*). Curve B: absorption of a mixture of ferric chloride (0.008 *M*) and resorcinol (0.08 *M*). Curve A: absorption of a mixture of ferric chloride (0.004 *M*) and resorcinol (0.04 *M*).

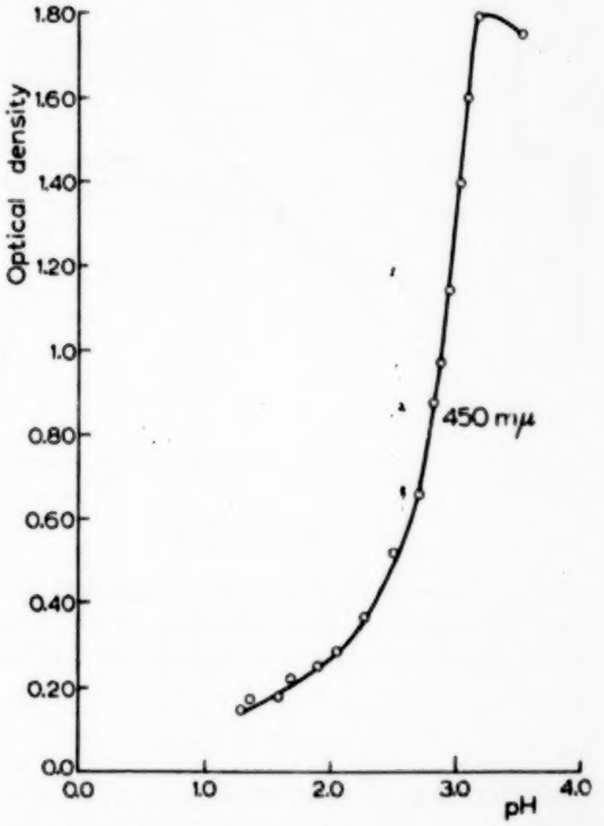

Fig. 2. Variation of optical density with pH of a mixture of ferric chloride (0.004 *M*) and resorcinol (0.04 *M*).

Composition

The composition of the coloured product was determined by following Job's continuous variation method[6] as modified by VOSBURGH AND COOPER[7]. Solutions of $M/60$ ferric chloride and $M/30$ resorcinol were mixed in different proportions in a total volume of 20 ml. The optical densities at different wavelengths, *e.g.* 450 and 540 mμ, were plotted against the composition of the solution, *i.e.*,

$$\frac{[\mathrm{R}]}{[\mathrm{R}] + [\mathrm{Fe}^{+3}]}$$

(Fig. 3). Both curves show maxima at a composition corresponding to 0.75, thus indicating the formation of a 1:3 product between ferric ion and resorcinol:

$$\mathrm{FeCl_3} + 3\,\mathrm{C_6H_4(OH)_2} \rightarrow \mathrm{Fe(C_6H_5O_2)_3} + 3\,\mathrm{HCl}.$$

An attempt to determine the composition by conductivity and pH titration methods failed to give conclusive results possibly because one of the reaction products is a free acid.

Beer's law

The validity of Beer's law for the system was investigated by the usual method at 450 mμ (Fig. 4). The system obeys Beer's law in the concentration range $0.25 \cdot 10^{-3}$ *M* to $1.416 \cdot 10^{-3}$ *M*.

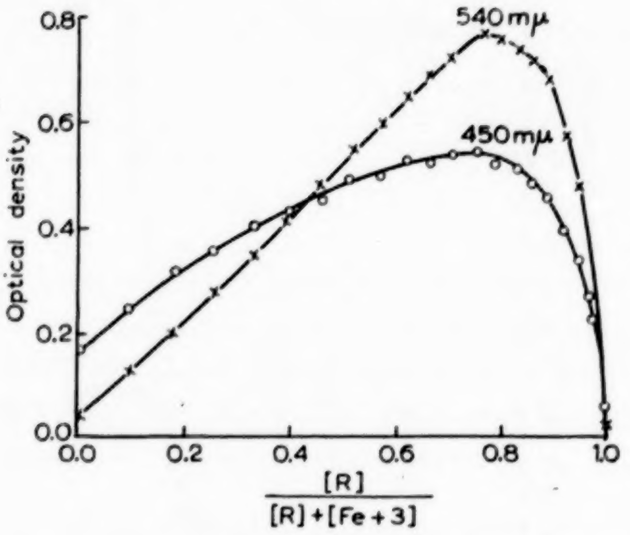

Fig. 3. Curves showing the composition of the coloured product formed from ferric chloride and resorcinol at 450 mμ and 540 mμ.

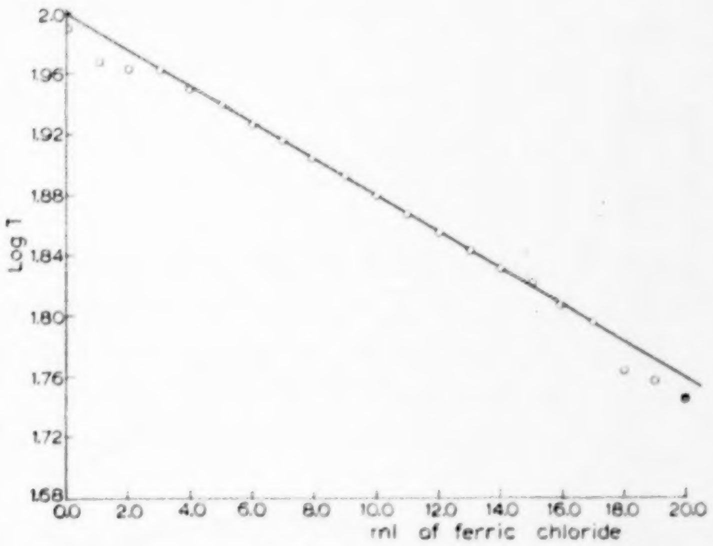

Fig. 4. Curve showing the validity of Beer's law for the system ferric chloride – resorcinol.

Interference of other ions

The effect of certain ions that are likely to interfere with the estimation of ferric iron was tested (Table I). The amount of an ion (in p.p.m.) that will produce a ± 2% change in optical density was taken as the tolerance limit.

TABLE I

EFFECT OF SOME CATIONS AND ANIONS

Ferric ion 0.00125 *M* (69.8 p.p.m.) and resorcinol 0.0125 *M*. Temp. 25–27°

Salts	*Ions*	*p.p.m.*	*% Change*	*Tolerance limit p.p.m.*
KCl	Cl^-	10,000	—2.2	10,000
KNO_3	NO_3^-	12,400	no change	large excess
K_2SO_4	SO_4^{-2}	4,800	—2.0	4,800
NaF	F^{-4}	1,900	—58.5	
		30	—23.5	
KBr	Br^-	8,000	+2.0	8,000
KI	I^-	6,350	—1.8	6,500
$KClO_3$	ClO_3^-	835	+2.3	835
$KBrO_3$	BrO_3^-	320	+3.2	
		200	+1.8	200
KIO_3	IO_3^-	12	+7	
$NaNO_2$	NO_2^-	1	+89	
$Na_2S_2O_3$	$S_2O_3^{-2}$	280	—2	280

TABLE I (continued)

Salts	*Ions*	*p.p.m.*	*% Change*	*Tolerance limit p.p.m.*
$K_2S_2O_8$	$S_2O_8^{-2}$	192	—17	
		10	+22	2
		2	+2.5	
Na_2CO_3	CO_3^{-2}	10	+30	
KCNS	CNS^-	2	+12	
$KMnO_4$	MnO_4^-	2	+56	
K_2CrO_4	CrO_4^{-2}	6	+65.5	
$K_2Cr_2O_7$	$Cr_2O_7^{-2}$	5	+45.6	
$K_3Fe(CN)_6$	$Fe(CN)_6^{-3}$	4	+82.3	
$K_4Fe(CN)_6$	$Fe(CN)_6^{-4}$	1	+18.5	
Na_2HAsO_4	AsO_4^{-3}	11	+9	
KH_2PO_4	PO_4^{-3}	72	—37.5	
		24	—12	
		2	—1.3	2
$(NH_4)_2MoO_4$	MoO_4^{-2}	6	+23	
		3	—22.0	3
$K_4Sb_2O_7$	$Sb_2O_7^{-4}$	1	+2.5	1
Na_2WO_4	WO_4^{-2}	5	+3	
		2	+2.1	2
K-formate	$HCOO^-$	11	+20	
Na-acetate	CH_3COO^-	150	—2.8	150
Na-oxalate	$C_2O_4^{-2}$	3	+5.7	
Na-K-tartrate	$C_6H_4O_6^{-2}$	37	+40	
		3	+5.7	
Na-succinate	$C_4H_4O_4^{-2}$	65	+30	
		22	+17.6	
		5	+1.9	5
Na-salicylate	$C_6H_4(OH)COO^-$	3	+60	
Na-citrate	$C_6H_5O_7^{-3}$	6	+2.0	6
$AgNO_3$	Ag^+	1	+20.7	
$CuSO_4$	Cu^{+2}	3	+3.4	
		2	+2.3	2
$HgCl_2$	Hg^{+2}	50	+4	
$SnCl_4$	Sn^{+4}	59	—8	
$BiCl_3$	Bi^{+3}	2	+51.3	
$CdCl_2$	Cd^{+2}	224	+4	
		112	+3.1	
		56	+2.4	50
$Al_2(SO_4)_3$	Al^{+3}	63	—2.3	
		13	+10	63
$CrCl_3$	Cr^{+3}	5	+4	
		3	+1.9	3
$Co(NO_3)_2$	Co^{+2}	2	+3	
		1	+1.5	1
$NiCl_2$	Ni^{+2}	2	+7	
		1	+3.1	1
$Ce(NO_3)_3$	Ce^{+3}	1	+3	1
$BeSO_4$	Be^{+2}	2	+2.0	2
$Th(NO_3)_4$	Th^{+4}	7	+8	
		1	+1.7	1

ACKNOWLEDGEMENT

The author expresses his grateful thanks to Prof. A. K. **BHATTACHARYA** for his kind interest in the present work, and to Mr. P. C. **JAIN** for his valuable assistance.

SUMMARY

A spectrophotometric method for a rapid determination of ferric iron with resorcinol is described. Ferrous iron has no effect.

RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage rapide du fer(III), au moyen de résorcine. Le fer(II) ne gêne pas.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Schnellmethode zur Bestimmung von Eisen(III) neben Eisen(II) mit Hilfe von Resorcin beschrieben.

REFERENCES

1 P. C. Jain and G. S. Rao, *Anal. Chim. Acta*, 20 (1959) 171.
2 S. M. Peach, *Analyst*, 81 (1956) 371.
3 M. Zehner, *Anal. Chem.*, 28 (1956) 198.
4 E. B. Buchanan and W. Wenger, *Anal. Chem.*, 29 (1957) 754.
5 A. L. Underwood, *Anal. Chem.*, 30 (1958) 45.
6 P. Job, *Ann. Chim.*, 9 (1928) 113.
7 W. C. Vosburgh and R. J. Cooper, *J. Am. Chem. Soc.*, 63 (1941) 437.

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SCHNELLE PAPIERCHROMATOGRAPHISCHE TRENNUNG VON Ba, Ca, Sr UND Mg

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EINLEITUNG

In der systematischen qualitativen Analyse der Kationen mittels Trennungen auf nassem Wege bietet bekanntlich die Gruppe der Erdalkalimetalle Schwierigkeiten, die durch die grosse Ähnlichkeit im chemischen Verhalten dieser Ionen verursacht werden. Eine sorgfältige Analyse dieser Gruppe erfordert denn auch relativ grossen Aufwand an Zeit und Mühe. Namentlich die Trennung von Ca und Sr ist gewöhnlich unbefriedigend. Für die bezüglichen Arbeitsmethoden sei auf die zahlreichen Bücher über qualitative Analyse verwiesen.

Die Möglichkeit einer papierchromatographischen Trennung wurde bereits von mehreren Autoren gezeigt. Die verschiedenen Arbeitsweisen unterscheiden sich *u.a.* mit Bezug auf die Papiersorte, das geradlinige oder radiale Laufen der mobilen Phase, die Zusammensetzung dieser Phase, die Zeitdauer vom Akklimatisieren des Papiers, die Dauer des Flüssigkeitsstromes und die Wahl der Nachweisreagenzien.

Auf der Suche nach einer Arbeitsweise die sich sowohl zum Unterrichtspraktikum als zu allgemeinen analytischen Zwecken eignen würde, stellten wir der zu wählenden

Methode folgende Anforderungen: leichte Durchführbarkeit mit einfachen Hilfsmitteln; kurze Dauer; gute Reproduzierbarkeit; genügend empfindlicher Nachweis jedes Ions auch neben relativ grossen Mengen der anderen, z.B. im Verhältnis 1:100. Keine der uns aus der Literatur bekannten Arbeitsweisen genügte all diesen Anforderungen gleichzeitig.

Im Laufe einer langen Reihe von Versuchen haben wir vielleicht alle in der Literatur empfohlenen Flüssigkeitsgemische, sowie die lineare und die zirkulare Chromatographie miteinander verglichen. Letztere Ausführungsform führte am schnellsten zum Ziel, und von den Laufmitteln ergaben die Gemische von Methylalkohol und Salzsäure[1], noch besser unter Zufügung von Tetrahydrofuran[2] weitaus die beste Kombination von schnellem Laufen und weiter, gleichmässiger Trennung der Zonen.

Das von uns benutzte Gemisch hatte die Zusammensetzung: 70% Salzsäure ($8N$), 20% Methylalkohol und 10% Tetrahydrofuran (Vol. %).

Die im Folgenden beschriebene Arbeitsweise entspricht dem oben genannten Zwecke.

ARBEITSWEISE

Aus dem Filtrat der Schwefelammongruppe werden die Erdalkalien einschliesslich Mg mittels Glühen mit Oxalsäure und Behandeln mit Ammonkarbonat nach SCHEINKMANN[3,4] als Karbonate erhalten, das Mg wohl zum Teil als Hydroxyd.

Nach Ausziehen der Alkaligruppe mit Wasser werden die Erdalkalikarbonate in der gerade benötigten Menge HCl $2\ N$ gelöst (Lösung A); von dieser Lösung wird mittels einer Mikropipette 1 μl auf eine Filterscheibe (S und S nr. 589^2) gebracht (Fig. 1, Punkt A). Der Rest der Lösung wird zur Trockne eingedampft und das Salz in einer äusserst geringen Menge Wasser (eventuell nur teilweise) zu einer möglichst grossen Konzentration gelöst (Lösung C). Auch von dieser Lösung, die also konzentrierter ist als A, wird 1 μl auf das Papier gebracht (Punkt C).

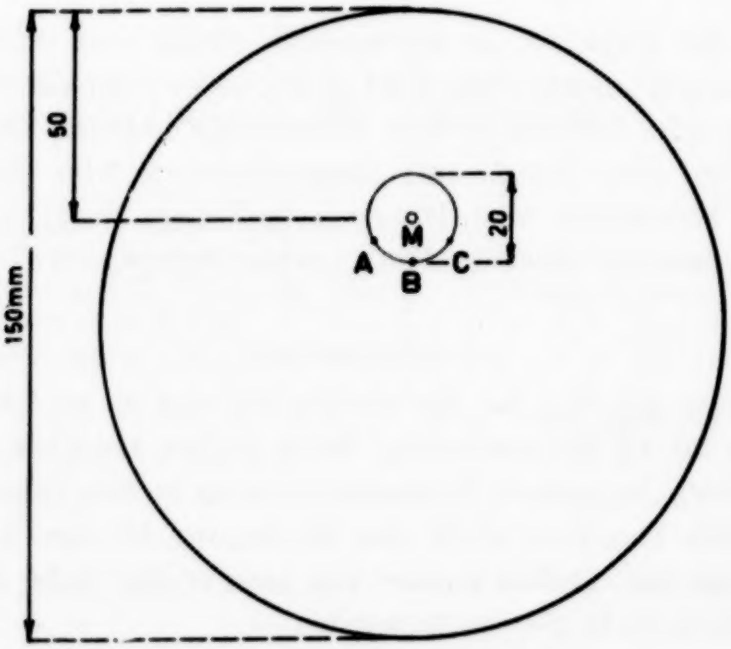

Fig. 1. Das Papier mit den Flecken.
A und C = Probelösung. B = Vergleichslösung. M = Loch mit Docht.

Die Anwendung von zwei verschiedenen Konzentrationen derselben Substanz hat den Vorteil dass in der verdünnteren Lösung die überwiegenden Komponenten keine zu breite Zonen bilden, während in der konzentrierteren der Nachweis der geringeren Komponenten verbessert wird.

Von einer Vergleichslösung, die die Chloride von Mg, Ca, Sr und Ba in einer Konzentration von 20 μg jedes Kations im μl enthält, wird gleichfalls 1 μl auf das Papier gebracht (Punkt B).

Die Punkte A, B und C liegen auf einem Kreise. Die Stellen und Abmessungen sind in der Fig. 1 ersichtlich. Im Mittelpunkt M des Kreises steckt ein Docht in einem Loch von 2 bis 3 mm Durchmesser; der Docht wird aus einem quadratischen Stückchen (15 × 15 mm^2) derselben Papiersorte gewickelt. Bekanntlich wird das Ergebnis des Versuches von der Dicke des Dochtes, also von der Intensität des Flüssigkeitsstromes, beeinflusst.

Das benötigte Gefäss ist äusserst einfach und wird aus drei Petrischalen zusammengestellt, wie aus Fig. 2 ersichtlich ist. In der abgebildeten schrägen Stellung der Schalen findet die Equilibrierung des Papiers statt; dies erfordert eine halbe Stunde, wonach das Ganze horizontal gestellt wird und das Chromatographieren anfängt, das $^3/_4$ Stunden dauert. Dann wird die Papierscheibe an der Luft, am besten mit Hilfe von Lampe oder Föhn, gut getrocknet.

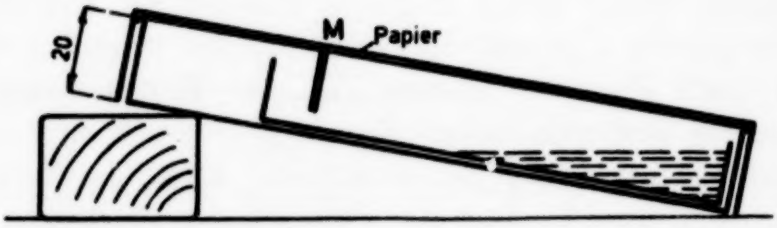

Fig. 2. Die Apparatur.

Zum Nachweis der Kationen ist der mobilen Phase von vornherein Oxin zugegeben (0.1 g in 100 ml); dieser Zusatz ist ohne einfluss auf die *R*-Werte. Die Zonen werden mit grüner oder bläulich grüner Fluoreszenz sichtbar wenn das getrocknete Chromatogramm auf eine Schale mit konzentriertem NH_3 gelegt und unter der Ultraviolettlampe beobachtet wird. Die einfache Philips Nr. HP 125 W genügte dem Zwecke ebenso gut wie eine Heraeus Analysenquarzlampe.

ERGEBNISSE

In der Reihenfolge Mg, Ca, Sr, Ba wurden für 100 R_e nachtstehende Werte gefunden: 38–44, 54–60, 64–72 und 81–85. Diese Zahlen beziehen sich auf die Mitten der Zonen, deren Tiefe bei grosser Konzentration bis 10 mm gehen kann. Die erzielte Gleichmässigkeit der Trennung stellt eine Bedingung für eine befriedigende Untersuchung der Gruppe dar: anders könnte von zwei relativ nahe aneinanderliegenden Zonen die schwächere leicht überdeckt werden.

Da die Werte von R_e, ausser von der Zusammensetzung der laufenden Flüssigkeit, auch von der Art des Papiers abhängig sind, ist es empfehlenswert bei Gebrauch

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einer anderen Papiersorte den gleichmässigen Verlauf der R_c Werte im voraus zu prüfen und nötigenfalls die Zusammensetzung der mobilen Phase anzupassen.

Die Anwendung der Vergleichslösung im mittleren Sektor erhöht die Sicherheit der Beobachtung schwacher Zonen und bietet auch einen Anhalt zur groben Schätzung der Mengen.

Die erreichten Empfindlichkeiten waren für Mg, Ca, Sr und Ba, in dieser Reihenfolge und bei direkter Verwendung van 1 μl Versuchslösung, also ohne vorhergehende Behandlung mit Oxalsäure und Ammonkarbonat:
1. beim Chromatographieren jedes Kations einzeln: 0.25, 1, 1 und 1 μg; 2. neben 100 μg irgendeines der andern drei Ionen: 0.25, 1, 1 und 1 μg; 3. neben je 50 μg von zwei der andern Ionen: 0.25, 1, 1 und 1 μg; 4. in gesättigter Lösung von $MgCl_2$, d.h. neben 120 μg Mg: —, 1, 1 und 1 μg; 5. in gesättigter Lösung von $CaCl_2$, d.h. neben 220 μg Ca: 1, —, 2 und 2 μg.

Die oben beschriebene papierchromatographische Arbeitsweise erlaubt also die Trennung und den Nachweis der Erdalkaliionen von Mg bis Ba mit guter Empfindlichkeit unter Verwendung einfacher Hilfsmittel und innerhalb einer Arbeitszeit.

Schliesslich sei noch erwähnt dass das Laufmittel am besten wöchentlich frisch bereitet wird. Mit älterer Flüssigkeit bekommen die Chromatogramme manchmal einen grün fluoreszierenden Hintergrund, der die Empfindlichkeiten wesentlich beeinträchtigt.

ZUSAMMENFASSUNG

Es wird eine zirkulare papierchromatographische Methode beschrieben zur schnellen Trennung und Identifizierung der Erdalkalien. Die mobile Phase besteht aus einem Gemisch von Methylalkohol, Salzsäure und Tetrahydrofuran, woran das Reagens Oxin zugefügt wird. Mit dieser Methode kann 1 μg jedwedes Kations in Gegenwart von insgesamt hundertfacher Menge der anderen drei Kationen nachgewiesen werden. Bei Mg ist die Empfindlichkeit 0.25 μg.

SUMMARY

A method for a rapid separation and sensitive detection of the alkaline earth cations by means of circular paper chromatography is described.

RÉSUMÉ

Une méthode est décrite pour la séparation rapide et pour l'identification sensible des cations alcalino-terreux, au moyen de la chromatographie circulaire sur papier.

LITERATUR

[1] G. SOMMER, *Z. anal. Chem.* 151 (1956) 336; 147 (1955) 241.
[2] H. HARTKAMP UND H. SPECKER, *Z. anal. Chem.*, 152 (1956) 107.
[3] C. J. VAN NIEUWENBURG UND J. W. L. VAN LIGTEN, *Kwalitatieve Chemische Analyse*, 4. Aufl. D. B. Centen, Amsterdam 1956, S. 185.
[4] A. SCHEINKMANN, *Z. anal. Chem.*, 83 (1931) 185.

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DETERMINATION OF PORPHYRINS IN CRUDE PETROLEUM

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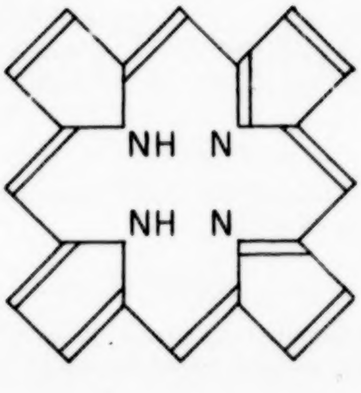
INTRODUCTION

The undesirability of certain trace metals and all nitrogenous compounds in petroleum fractions that are to be catalytically refined is well known. Metals deactivate cracking and other catalysts[1], and nitrogen compounds impair both the activity of catalysts[2] and the stability of refined products[3]. Certain metals are known to be bound, at least in part, to the nitrogens in the large porphyrin molecules in crude oil. Such stable metal porphyrins as those of vanadium and nickel have also been found in distillates. In view of the relationship of porphyrins to these problems, a rapid method for determining porphyrin content would be useful. It would also be helpful in studies of the origin of petroleum.

Porphyrins are a class of compounds consisting of four condensed pyrrol rings having the general structure:



The different porphyrins are formed by the substitution of different organic side-chains on the periphery of the large ring. Their spectra all show similar absorption maxima in the visible region. A chloroform solution of porphyrins shows a maximum absorption peak at 500 mμ, which provides a convenient basis for a quantitative spectrophotometric method for determining porphyrins.

Although the general techniques were established earlier by TREIBS[4], only one method has been published for the quantitative determination of porphyrins in crude petroleum. In the method of GROENNINGS[5] the porphyrins are freed from their metal complexes by treatment, in sealed ampoules for four days, with glacial acetic acid saturated with hydrogen bromide. Oil impurities are removed from the diluted acid–porphyrin solution by repeated transfer between ether and 7% hydrochloric acid. Quantitative colorimetric measurement of the porphyrins is made in chloroform solution.

A shorter, simpler, and more accurate procedure has been developed for determining porphyrins in crude petroleum. The acid reagent and the petroleum are reacted in an open flask, as used in extracting metals from petroleum distillates[6]. The crude porphyrins are purified by a simple and rapid filtration and recovered quantitatively.

METHOD

The reagents are conventional, except for an acetic acid–hydrogen bromide reagent, which may be purchased or prepared by saturating glacial acetic acid at 0° with anhydrous hydrogen bromide. The procedure for extracting and measuring the porphyrins is as follows:

Conduct the extraction in a hood using the apparatus shown in Fig. 1. Dilute 50 g of crude petroleum with an equal volume of benzene, and transfer into the extraction flask. Add a volume of glacial acetic acid–hydrogen bromide reagent equal to that of the oil. Stir the mixture for six hours at 45° and then transfer it to a separatory funnel containing about 75 g of crushed ice. Rinse the extraction flask with small amounts of benzene, and add the rinsings to the separatory funnel. Without shaking, let the mixture stand until the oil and aqueous phases have distinctly separated.

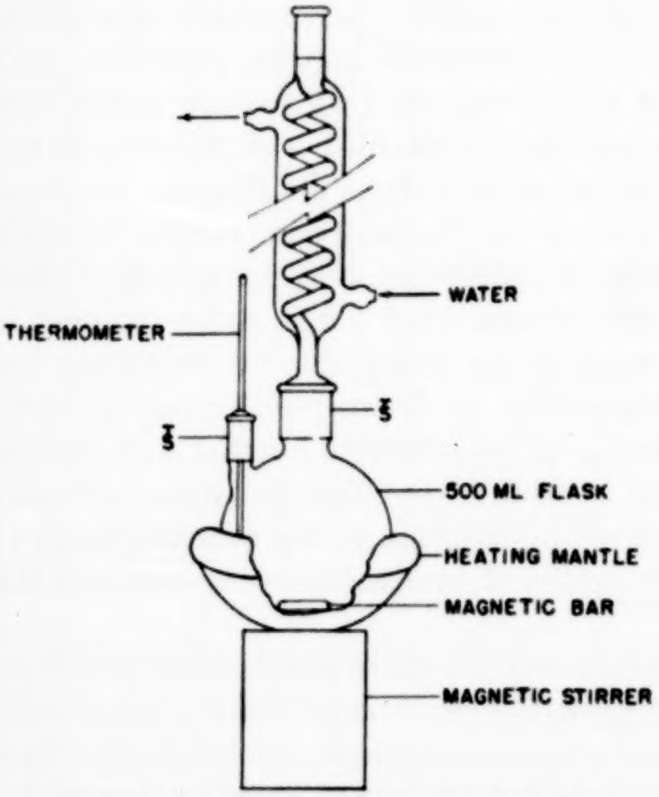


Fig. 1. Apparatus for the extraction of porphyrins from crude oil.

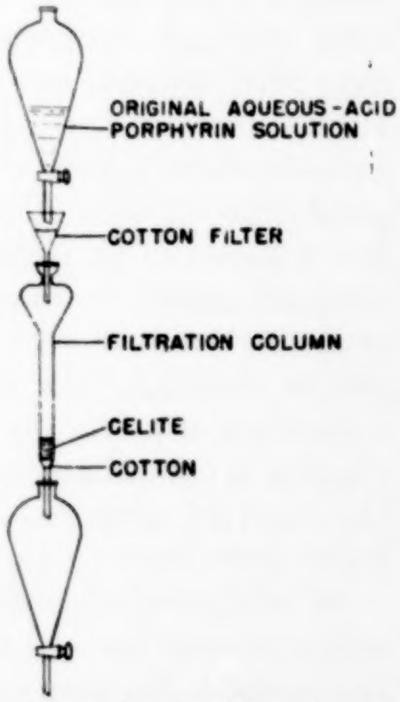


Fig. 2. Apparatus for the removal of oil impurities from acid–porphyrin solution.

As diagrammed in Fig. 2, filter the red aqueous–acid phase through cotton directly into the filtration column. Shake the oil phase gently with 25 ml of 20% hydrochloric acid to extract any remaining porphyrins. Pass the acid wash through the cotton filter, and discard the oil. Wash the cotton free of porphyrin solution with a small amount of 20% hydrochloric acid. Hasten the filtration of the combined acid–

porphyrin solution through the Celite by applying slight air pressure, and receive the filtrate in a separatory funnel. (Mesh size of the Celite is immaterial, but it must be washed thoroughly with 20% hydrochloric acid before use.) Wash the bed of Celite free of red porphyrin solution with small amounts of 20% hydrochloric acid, and combine the washings with the acid–porphyrin solution.

Extract the porphyrins from the combined acid solutions with 25-ml portions of reagent-grade chloroform. Continue the extractions until the extract shows no red color. Use a pocket spectroscope to check either the acid or chloroform phases for completeness of extraction.

Remove all traces of acid from the chloroform extract by washing five times with an equal volume of distilled water. To remove traces of water, filter the chloroform solution through cotton wetted with chloroform. Receive the filtrate in a 500-ml volumetric flask, and dilute to volume.

Measure the absorbance at 500 mμ of the porphyrin solution against chloroform as a blank in a suitable spectrophotometer with a tungsten light source. Determine the concentration of porphyrin from a calibration curve.

Prepare the calibration curve from porphyrins isolated from crude petroleum. Because the porphyrin content of a given crude petroleum may be unknown, continue thorough extractions of quantities of the petroleum until enough porphyrins have been obtained for preparing standard solutions to establish a calibration curve; a stock solution of 20 mg of porphyrins in 100 ml of chloroform is sufficient. Combine the chloroform solutions and distill off the chloroform. To purify the residue of crude porphyrins, dissolve it in a minimum volume of chloroform and precipitate it with five volumes of 95% methanol[5]. Repeat this process until a non-sticky product is obtained (about 10 times). Estimate the purity of the porphyrins by comparing the elemental analysis with the per cent composition of desoxyphyllerythro-etioporphyrin, $C_{32}H_{36}N_4$, the predominant porphyrin in petroleum[4]. Further aids to the estimation of purity are melting point, and a study of the absorptivity of the porphyrins in chloroform solution. Apply the purity correction to the concentrations of the standard solutions, and plot their absorbances *vs.* concentration to establish the linear calibration curve.

No study was made of the necessity of preparing the calibration curve from crystalline porphyrins, and a valid curve could probably be obtained from a noncrystalline product. The numerous recrystallizations required to obtain a non-sticky product would be eliminated, and the resulting calibration curve would be more representative of the porphyrins being measured.

TABLE I

EFFECT OF TIME ON FLASK EXTRACTION OF PORPHYRINS

Extraction time, h	*Porphyrins p.p.m.*
4	284
5	291
6	312
6	302
7	305
24	312
96	304

DEVELOPMENT OF METHOD

Development of the present method resulted from a detailed investigation of previously published techniques[4,5] for determining porphyrins. Lagunillas (Venezuela) crude petroleum was used in these studies.

Determination of porphyrins in this petroleum by the GROENNINGS'[5] method showed a content of 303 p.p.m. With the sole modification of the extraction flask for the ampoule in the GROENNINGS' method, the same amount of porphyrins was extracted and the extraction was completed in six hours, as shown in Table I. Although the extraction time in the ampoule method could also be shortened, the flask is far more convenient than the sealed ampoule. A shorter reaction time in the ampoule has been recently confirmed[7].

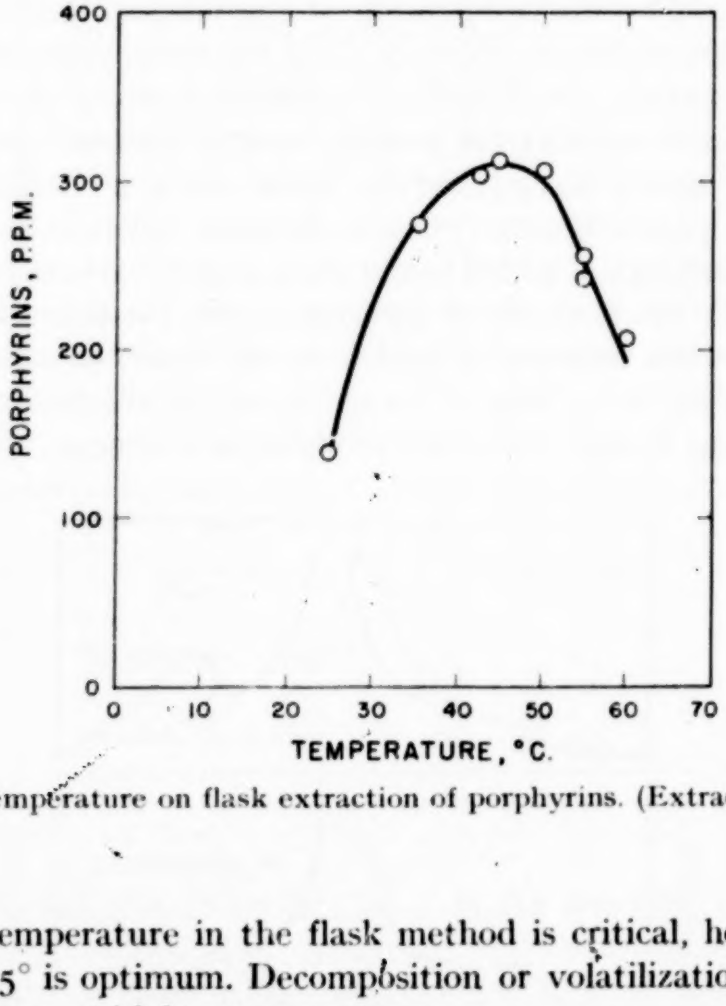


Fig. 3. Effect of temperature on flask extraction of porphyrins. (Extraction time: 6–8 h).

The extraction temperature in the flask method is critical, however, and Fig. 3 shows that about 45° is optimum. Decomposition or volatilization may account for the decreased recovery at higher temperatures.

Oil impurities in the aqueous acid–porphyrin solution are removed in the latter stages of purification in the GROENNINGS' method by transferring the porphyrins twice between 7% hydrochloric acid and ether. As expected[9] absorption spectra of the ether solutions from which porphyrins were extracted by 7% hydrochloric acid showed that not all of the porphyrins are removed. Higher concentrations of hydrochloric acid, however, extract porphyrins from ether solution quantitatively[8,9]. Data in Table II show the additional amounts of porphyrins extracted by 20% hydrochloric acid. Thus, in the case of Lagunillas crude, purification of the porphyrins by transfer between 7% hydrochloric acid and ether loses about 39 p.p.m. of the porphyrins, or about 13% remains in the ether solutions.

TABLE II

PORPHYRINS LEFT IN ETHER BY 7% HCl, BUT EXTRACTED BY 20% HCl, p.p.m.

1st Ether solution	*2nd Ether solution*	*Total*
26	7	33
11	11	22
32	17	49
36	8	44
31	14	45
	Average	39

The tedious and time-consuming transfers between acid and ether are eliminated in the present method by direct filtration of the original acid solution through a column of Celite. This technique recovers all of the porphyrins and removes oil impurities more conveniently. Quadruplicate determinations of the porphyrin content of Lagunillas crude petroleum by the present method showed 347, 355, 322, and 336 p.p.m., with an average of 340 p.p.m. The results show a standard deviation of 12 p.p.m. When the 39 p.p.m. of porphyrins in the ether which is not extracted by 7% hydrochloric acid (Table II) is added to the 303 p.p.m. measured by the GROENNINGS' procedure, the results are in excellent agreement with the present method.

The need for complete removal of acid from the final chloroform solution of the porphyrins was revealed in a study of the spectra of the chloroform solution at different stages of washing. Except for a shift to higher wavelengths, the absorption spec-

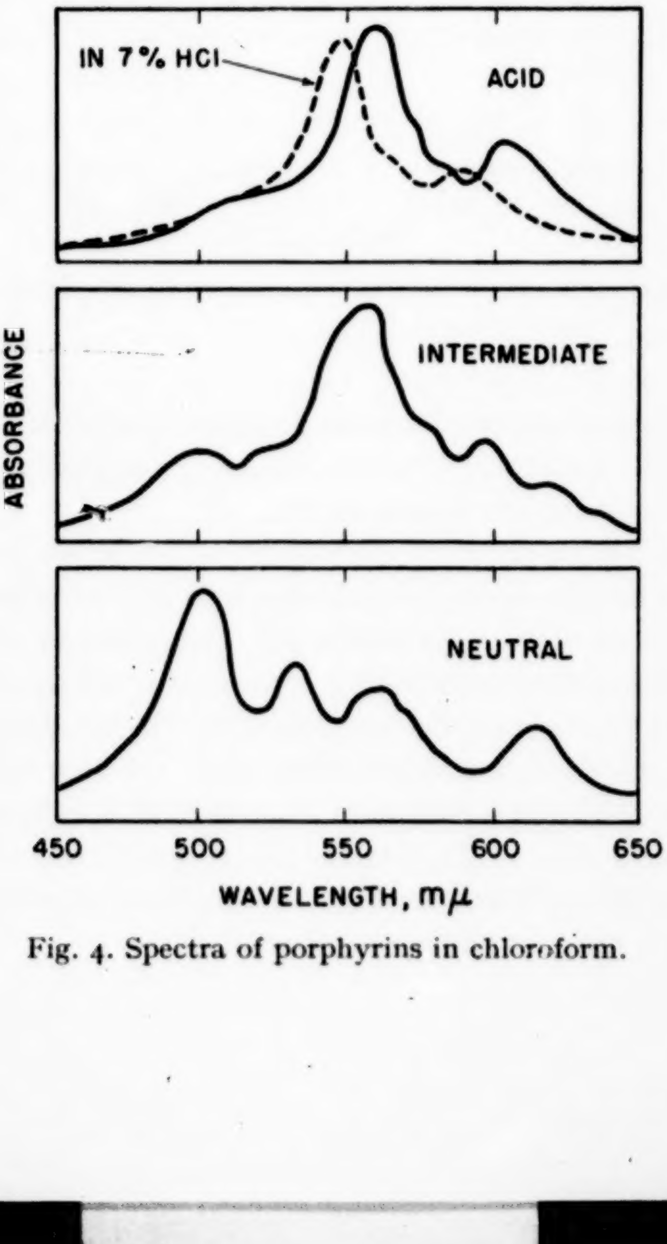


Fig. 4. Spectra of porphyrins in chloroform.

trum of the unwashed chloroform solution showed the two absorption peaks exhibited by acid solutions of porphyrins[10]. Thorough water-washing of the chloroform solution results in a characteristic four-peaked spectrum[11]. The changes in absorption spectra, illustrated in Fig. 4, are reversible simply by the addition or removal of acid. The center absorption curve represents an intermediate spectrum between the acid and neutral forms. Over a two-week period, the absorbance of a chloroform solution of porphyrins washed 10 times decreased from 0.400 to 0.359. The decrease in absorbance probably results from the presence of hydrogen chloride produced by the decomposition of chloroform. The spectral changes result from shifts in the equilibrium between the neutral and protonated forms of the porphyrin molecules and are separate and distinct from changes in spectra resulting from chemical decomposition of the porphyrins[8,12]. If PH_2 is considered as the neutral porphyrin molecule, the equilibria may be represented as:

$$PH_2 + H^+ \rightleftarrows PH_3^+$$
$$PH_3^+ + H^+ \rightleftarrows PH_4^+$$

The four nitrogens in the porphyrin ring have been shown to participate in a series of acid–base equilibria[13]. Solutions of porphyrins in varying concentrations of hydrochloric acid up to 20% showed no change in absorbance. To insure that no significant decrease in absorbance occurs in the chloroform solution washed five times in the routine method, the porphyrins should be stored in the filtered acid solution if optical measurements can not be made within a day.

TABLE III

EFFECT OF IMPURITIES ON THE DETERMINATION OF PORPHYRINS IN ACID SOLUTION

Purification	*Porphyrins p.p.m.*	
	Acid	*$CHCl_3$*
Groennings' method	374	324
	383	331
Present method	414	347
	400	322
	399	336

The existence of a suitable absorption peak in the spectrum of acid solutions of porphyrins suggested the possibility of further shortening the present method, by eliminating the transfer of the porphyrins into chloroform and the subsequent water washing of the chloroform solution. Table III shows, however, that purification of porphyrins by either the GROENNINGS' method or the present method resulted in higher apparent concentrations of porphyrins when measured in acid solution than when measured in chloroform. The discrepancy is believed due to an impurity in the acid phase. Until the nature of the impurity and a convenient method for removing it are found, the porphyrins must be transferred into chloroform for accurate determination.

CONCLUSION

Because of its simplicity, the present method lends itself to multiple routine analysis. Although this investigation was limited to Lagunillas crude petroleum, the

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method may be applicable to many other crudes, reduced crudes, and petroleum fractions, as well as to other fields of study where quantitative knowledge of porphyrins is needed.

SUMMARY

The method of GROENNINGS for determining porphyrins in crude petroleum, based on extraction with glacial acetic acid–HBr, has been simplified, shortened, and improved in precision and accuracy. Porphyrins are extracted at atmospheric pressure, and the extract is purified by filtration through Celite. Extraction and spectrophotometric determination of the porphyrins can be completed in a single day. The method has a standard deviation of 12 p.p.m. in the 300 p.p.m. range. The normal four-peaked spectrum of porphyrins in chloroform is converted in time to the two-peaked acid spectrum. The change is reversible and results from a shift in the equilibrium between the free base and the protonated porphyrin molecule. This behavior is distinct from changes brought about by decomposition of the porphyrin.

RÉSUMÉ

L'auteur propose une modification de la méthode de GROENNINGS pour le dosage des porphyrines dans le pétrole. Cette nouvelle technique est plus simple, plus rapide et permet d'obtenir une précision meilleure. On procède à une extraction au moyen du mélange acide acétique–acide bromhydrique, puis à une extraction dans le chloroforme et finalement au dosage spectrophotométrique de la porphyrine extraite.

ZUSAMMENFASSUNG

Es wird eine vereinfachte, kürzere und mit grösserer Genauigkeit arbeitende Modifikation der Methode von GROENNINGS zur Bestimmung der Porphyrine im Erdöl beschrieben. Die Porphyrine werden mit einem Bromwasserstoff–Eisessig Gemisch extrahiert und in Chloroform spektrophotometrisch bestimmt.

REFERENCES

[1] R. A. WOODLE AND W. B. CHANDLER, JR., *Ind. Eng. Chem.*, 44 (1952) 2591.
[2] G. A. MILLS, E. R. BOEDEKER AND A. G. OBLAD, *J. Am. Chem. Soc.*, 72 (1950) 1554.
[3] R. B. THOMPSON, J. A. CHENICEK, L. W. DRUGE AND T. SYMAN, *Ind. Eng. Chem.*, 43 (1951) 935.
[4] A. TREIBS, *Ann.*, 510 (1934) 42.
[5] S. GROENNINGS, *Anal. Chem.*, 25 (1953) 938.
[6] J. E. BARNEY, II, *Anal. Chem.*, 27 (1955) 1283.
[7] J. W. MOORE, AND H. N. DUNNING, *Report of Investigations 5370*. Bureau of Mines, Bartlesville, Oklahoma, U. S. Dept. of the Interior, Nov. 1957.
[8] H. N. DUNNING, J. W. MOORE AND A. T. MYERS, *Ind. Eng. Chem.*, 46 (1954) 2000.
[9] A. TREIBS, *Ann.*, 517 (1935) 172.
[10] H. FISCHER AND H. ORTH, *Die Chemie Des Pyrrols*, Vol. II, Akad. Verlag, Leipzig 1940, p. 579.
[11] R. LEMBERG AND J. W. LEGGE, *Hematin Compounds and Bile Pigments*, Interscience Publishers, New York 1949, pp. 74, 94.
[12] H. N. DUNNING, J. W. MOORE AND H. O. DENEKAS, *Ind. Eng. Chem.*, 45 (1953) 1759.
[13] R. I. WALTER, *J. Am. Chem. Soc.*, 75 (1953) 3860.

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A SYSTEM FOR THE ANALYSIS OF NITRATES AND OXIDES OF NITROGEN*

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In this laboratory, it has been necessary to construct a system for the analysis of oxides of nitrogen in a study concerning the decomposition of metal nitrates and the interaction of NO_2 with metal oxides. With this system it is possible to determine the absolute amounts of NO_2, N_2O_3, NO, and of either N_2O or mixture of N_2 and O_2, simultaneously present in the gas phase. It is also possible, by prior thermal decomposition, to analyze the nonvolatile metal nitrates and nitrites.

The design is partially based upon work by MEYER AND VOOGEL[1] in which it was reported that metallic nickel at moderate temperatures retains the oxygen component in the oxides of nitrogen. It has been possible to adapt and modify the procedure of MEYER AND VOOGEL to yield quantitative results.

The method of analysis

The system consists of five major parts: the reaction chamber, the nickel–nickel oxide tube, the pumping and manometering section, and two purification sections. The sample to be analyzed is placed in the reaction chamber (Y) of Fig. 1. The entire system is then evacuated to a pressure of 10^{-6} mm of Hg. This eliminates the possibility of analyzing compounds that are volatile at room temperature. The sample is then thermally decomposed. For materials that tend to volatilize preceding decomposition, a heated silver or platinum gauze was placed in the mouth of the reaction chamber. This insures that decomposition of the metal nitrate is complete. Precautions must then be taken to remove the oxide coating on the gauze. The decomposition products now pass toward cold trap (G). By cooling this trap with liquid nitrogen, it is possible to separate the NO_2–N_2O_3 components from the more volatile NO (present only if originally in excess of NO_2), and the N_2O or N_2–O_2 mixture. The latter gases now pass to the tube H, which consists of nickel supported upon asbestos.

The impregnated asbestos is prepared by saturating with nickel ammine nitrate, and igniting the saturated asbestos in a nickel crucible at 800°. This powder is then packed into a vycor or quartz tube and reduced with hydrogen. In order to assure complete removal of the oxygen components from the nitrogenous gases, the nickel asbestos mixture must be heated to 800°. The resultant nitrogen now passes through the cold trap J which is cooled with liquid nitrogen, thence to the pump K^2 and to the manometer M, which is depicted in Fig. 2. The volume of the upper bulb is internally calibrated by introducing known quantities of hydrogen at given pressure and temperature. Knowing the volume, the amount of nitrogen transferred through the Toepler pump is determined from the residual pressure in the bulb.

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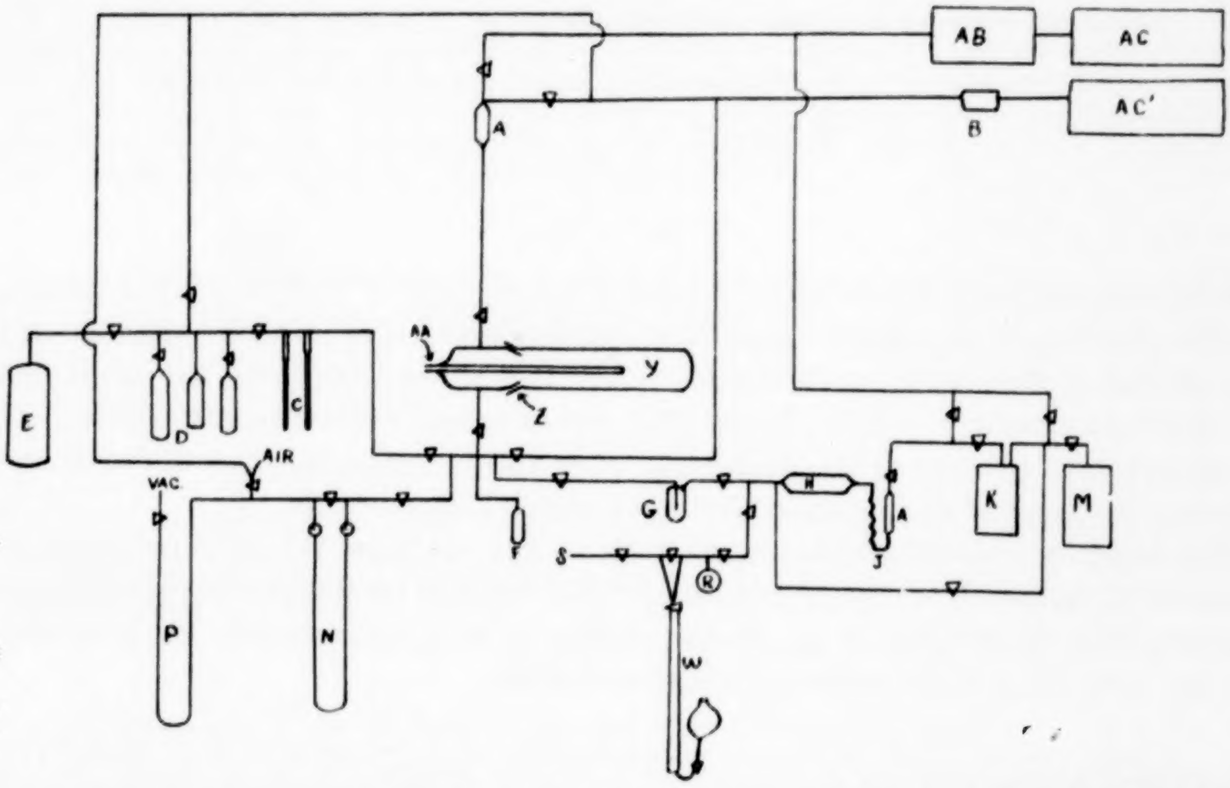

Fig. 1. Diagram of vacuum line for N-O analysis. A = Copper isolation trap, B = NO_2 catch trap, C = micro pipettes (0.1 and 1.0 ml), D = NO_2 storage - and purification, E = tank NO_2, F = finger trap, G = NO_2–N_2O separation trap, H = Ni–NiO tube, J = water trap, K = modified Toepler pump, M = volumetric manometer, N = oil manometer, P = mercury manometer, R = ballast, S = pure H_2. Pt–Pd thimble, W = volumetric H_2, Y = reaction tube, Z = 29/42 ₮ joint, AA = thermocouple well, AB = annular Jet Diffusion Pump, AC = fore pump – 10^{-3} mm, AC′ = fore pump – 1 mm, ▽ = vacuum bulb stopcock 4 mm, except on NO_2 system where Teflon plug stopcocks are used.

The nitrogen sample is now removed by means of pumps AB–AC and hydrogen is admitted to the Ni–NiO mixture in tube H, maintained at 800°. The water vapor formed by reduction of NiO is trapped in J and the excess hydrogen passes to the pump K. In order to assure complete reduction, the hydrogen is circulated by means of this pump through the tube H. The hydrogen is finally transferred to M and metered. The mole quantities of N_2 and H_2 are computed and the mole quantity of O is deduced. The procedure is then repeated for nitrogen oxides condensed in trap G.

In order to purify and meter NO_2 and H_2 separate sections C-D-E, and S were constructed. NO_2 is purified by repetitive distillation and stored in D. H_2 is purified by diffusion through a heated platinum–palladium thimble and stored in S. NO_2 is metered by means of the volumetric pipettes C. H_2 is manometered into (H) by means of a burette (W) graduated in units of 1/10 ml. In employing a 50-ml gas sample, the volume is therefore determined to about 0.2%.

All gas samples pass through the tube H at a very low flow rate at moderate pressures because of the tight packing of the solid in this tube. At the temperature of operation the reduction of nitrogen oxide is quantitative under these conditions; however, the reduction of NiO by H_2 requires some care, because sufficient time must be allowed for H_2O to transfer to trap J. As will be shown later, it is desirable to circulate the H_2 repeatedly through tube H to remove all traces of moisture from the tube.

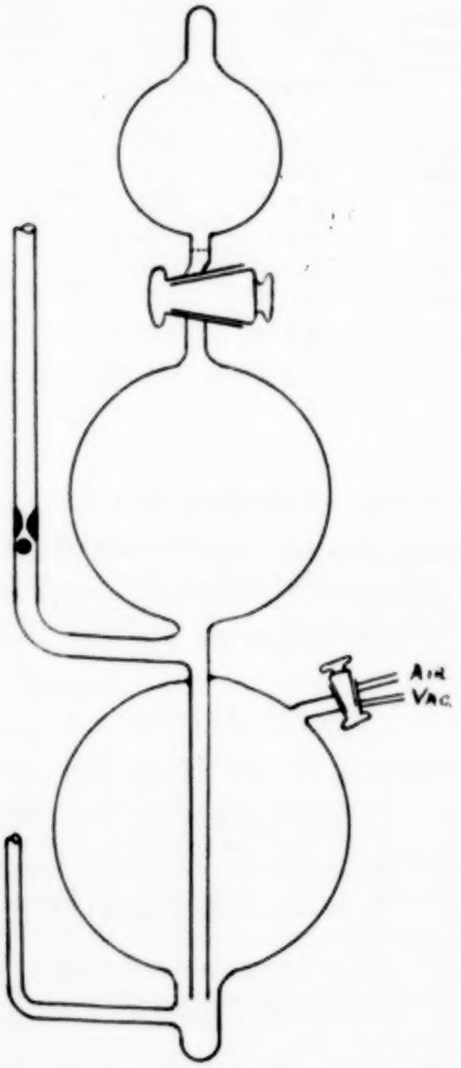

Fig. 2. Combination Toepler pump and manometer.

RESULTS AND DISCUSSION

A rather careful study of the factors affecting the analysis was carried out, using highly purified NO_2 as a test material. In order completely to reduce the nitrogen oxides, and to carry out the subsequent reduction with H_2, it was necessary to maintain the nickel powder at 800°. Further, an excess of H_2 is required and it was necessary to await quantitative diffusion of H_2O into trap J or to circulate the H_2 gas by means of pump K. The relevant factors are summarized in Tables I and II. It is to be noted that at a temperature of 400°, less than half of the oxide was reduced. As the reduction temperature is increased, there is a progressive approach to the proper O/N ratio of two. If, at 800°, H_2 gas was allowed to pass to M without holding it at H

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over an extended period of time, the result was a low O/N mole ratio (1.872). As the retention time at H was increased to 1/2 h, the O/N mole ratio exceeded 1.9, while for a 1-h period this ratio approached the proper stoichiometric value. A similar result could be obtained by circulating H_2. This method proved the most effective.

TABLE I

Volume of N_2 found in cc at standard temperature and pressure	*Ratio H/N*	*Ratio O/N*	*Temperature of reduction in °C*
40.413	1.616	0.81	400
23.982	2.648	1.33	450
38.777	3.26	1.63	500
15.561	3.22	1.615	550
48.197	3.795	1.897	700
49.501	3.948	1.973	800
38.739	4.124	2.062	800

TABLE II

RATIO O/N FOR VARIATION IN MODE OF REDUCTION OF NiO IN THE ANALYSIS OF NO_2
(Tube H at 800°)

Volume of N_2 found in cc at standard temperature and pressure	*Ratio H/N*	*Ratio O/N*	*Comments*
58.591	3.643	1.872	Hydrogen immediately passed to M
66.749	3.826	1.913	Hydrogen admitted to H and held for 1/2 h preceding pumping
25.971	4.0125	2.006	Hydrogen admitted to H and held 1 h preceding pumping
12.379	4.091	2.046	Hydrogen admitted to H and held 1 h preceding pumping
38.739	4.124	2.062	Hydrogen admitted to H and held 1 h preceding pumping
64.312	3.856	1.928	Sample circulated through H by pump K
17.139	4.019	2.009	Sample circulated through H by pump K

The decomposition of three solid nitrates was studied; Table III summarizes the results. Barium nitrate was heated to 900°; at this temperature, the nitrate is converted to BaO[3] and consequently the ratios I/III and II/III should be 2 and 5. These compare favorably with the observed results. The results are slightly low due to partially adsorbed and occluded water.

Lead nitrate was decomposed at 900°. Under these conditions, it should form PbO[3]. If the oxide is further reduced to Pb by means of H_2, the ratios I/III and II/III should be 2 and 6 respectively. The first ratio is again slightly low, due to the presence of H_2O. The second ratio is closer to 5 due to partial reaction of PbO with the silica container, giving $PbSiO_3$.[3] It was observed that the quartz vessel disintegrated at the conclusion of the run. Had the reaction been complete, the expected II/III ratio would have been 5.

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Ammonium nitrate was decomposed at temperatures in the range 200–400°. However, to assure complete decomposition of the relatively volatile material, the gases were passed over silver gauze maintained at 700°. At higher temperatures, the silver was markedly oxidized by the N_2O gas. It was therefore necessary to include the silver in the reduction step. Quite satisfying results were obtained.

TABLE III

ANALYSIS OF NITRATES

Nitrate	*I* *Moles (N)* $x \cdot 10^3$	*II* *Moles (O)* $x \cdot 10^3$	*III* *Moles nitrate* $x \cdot 10^3$	*Ratio*	
				I/III	*II/III*
$Ba(NO_3)_2$	3.242	8.030	1.623	1.936	4.949
$Pb(NO_3)_2$	3.699	9.806	1.902	1.944	5.155
NH_4NO_3[a]	2.127	1.268	1.247	1.017	1.706
NH_4NO_3	2.757	1.392	1.374	2.006	1.013
NH_4NO_3	3.886	1.928	1.903	2.042	1.013

[a] Silver gauze oxidation not included.

The above results indicate that the procedure, under carefully controlled conditions, yields correct results and that the procedure may be applied in confidence. Further work on the thermal decomposition of metallic nitrates and studies in the interaction of NO_2 with metallic oxides are under way[4].

ACKNOWLEDGEMENT

The author wishes to express thanks to Dr. J. M. HONIG for his constant interest in this work and to Mr. Q. CHOI for his suggestions.

Thanks are due to the National Sciences Foundation for a grant G5122 under which the testing of the equipment was completed.

SUMMARY

A system for the analysis of oxides of nitrogen and metal nitrates is presented. The factors affecting the analysis are tested by analyses of NO_2, and various nitrates.

RÉSUMÉ

Une méthode est proposée pour l'analyse des oxydes d'azote et des nitrates métalliques.

ZUSAMMENFASSUNG

Es wird ein Verfahren beschrieben zur Analyse von Oxyden des Stickstoffs und Metallnitraten.

REFERENCES

[1] G. MEYER AND P. VOOGEL, *Rec. trav. chim.*, 70 (1951) 833.
[2] F. VRÁTNÝ AND B. GRAVES, *Rev. Sci. Instr.*, 30 (1959) 296, 597.
[3] A. GLASSNER, *The thermochemical properties of the oxides, fluorides, and chlorides to 2500° K*, ANL 5750, U.S.A.E.C.
[4] F. VRÁTNÝ AND J. M. HONIG, to be published.

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SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM WITH 9-METHYL-2,3,7-TRIHYDROXY-6-FLUORONE

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Titanium(IV) in acid solutions forms a rose-red complex with methyl fluorone, in the same way as molybdenum(VI). The colour reaction is very sensitive; a spectrophotometric method for the determination of traces of titanium is described in this paper.

Amongst the several spectrophotometric methods[1], that using hydrogen peroxide[2-4] is most favoured because of its simplicity and relative freedom from interference. Its low sensitivity, however, necessitated studies of other methods *e.g.* dihydroxymaleic acid[5], tiron[6] and chromotropic acid[7]. The last reagent is more sensitive than the others but is highly photosensitive and needs accurate pH control. Recently the very sensitive phenyl fluorone has been applied[8].

The reaction of methyl fluorone with titanium is very similar to that with molybdenum[9] and the titanium complex has the same tendency to precipitate out of the acid solution unless peptised and kept in solution by gelatin in presence of 12% ethanol. The colour formed is quite suitable for spectrophotometric measurements and shows maximum intensity between pH 1.7 and 2.1, with maximum absorption at 520 mμ. The system obeys Beer's law from 0.025 to 0.6 p.p.m. of titanium, but the optimum range is from 0.1 to 0.6 p.p.m. of titanium, where the percentage analysis error per 1% absolute photometric error is 3.1. JOB's method of continuous variation and the molar ratio method indicate that in solution the complex contains the metal and the reagent in the ratio of 1:2. The molar extinction coefficient of the complex is 60360 and the instability constant is $1.6 \cdot 10^{-12}$ determined at 20°.

EXPERIMENTAL

Apparatus and solutions

The Uvispek spectrophotometer with 10-mm quartz transmission cells, and the pH indicator were the same as in the previous work[9].

Titanium solution: About 26.0 g of potassium titanium fluoride were fumed with pure sulphuric acid and the resulting sulphate was dissolved and made up to 1 l with water. The final solution was about 5 *N* in sulphuric acid. The titanium content per ml of the solution was determined gravimetrically. Weaker solutions were made as required by dilution.

A 0.025% (w/v) solution of methyl fluorone, and a sodium acetate–hydrochloric acid buffer pH 2 were prepared as in the previous work. A 0.4% (w/v) solution of gelatin, and equimolecular solutions of titanium were also prepared.

Spectral transmittancy: To a 50-ml beaker were added successively an aliquot of the titanium solution, 1 ml of the gelatin solution, 3 ml of the reagent and 2 ml of absolute alcohol. The pH was adjusted to 2 with *N* sodium acetate and the solution transferred to a 25-ml flask; 3 ml of the buffer solution were added and the solution was made up to 25 ml with distilled water. Simi-

larly a reagent blank without titanium was prepared. The test solution contained 0.25 p.p.m. of titanium. The optical densities of the test and the blank solutions were measured against distilled water at various wavelengths from 480 to 600 mμ. The spectral transmittancy curves are shown in Fig. 1. At 520 *m*μ, the complex shows maximum absorption against the reagent blank, and this wavelength was chosen for all further work.

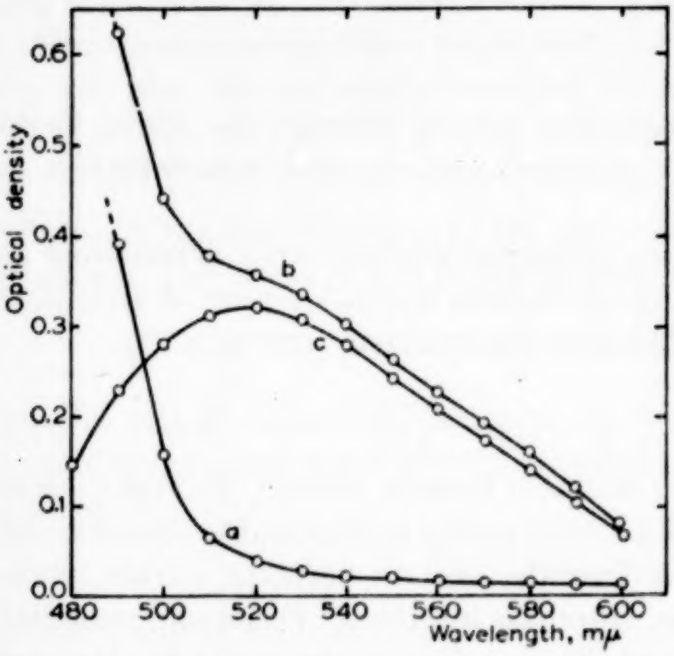

Fig. 1. Spectral transmittancy curves: (a) Reagent against water. (b) Reagent plus titanium against water. (c) Reagent plus titanium against reagent.

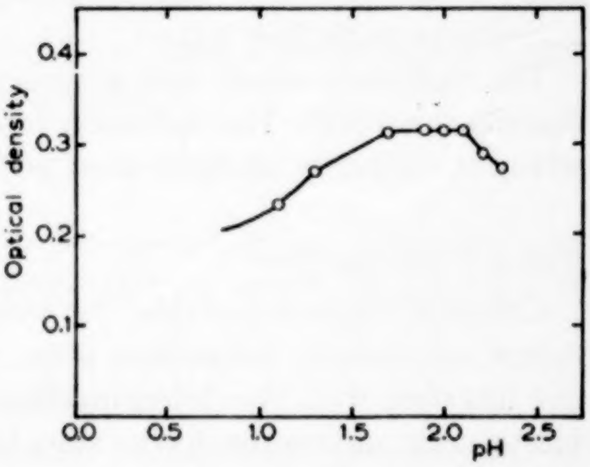

Fig. 2. Effect of pH.

Effect of pH, reagent and time

For the study of the effect of pH, the pH of the test and the reagent solutions was altered by suitable addition of *N* sodium acetate or *N* sulphuric acid. The change of absorption with respect to the reagent blank at various pH values is shown in Fig. 2. The readings were quite constant within the range 1.7–2.1 which was used for subsequent work. Above pH 2.3, the titanium complex precipitated even in presence of gelatin and alcohol.

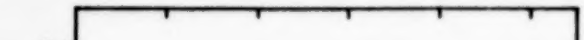

Fig. 3. Effect of reagent.

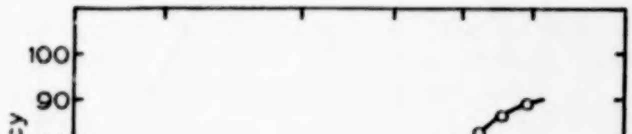

Fig. 4. Standard curve for titanium–methylfluorone complex.

The variation of O. D. with increasing amounts of reagent is shown in Fig. 3; 2 ml of 0.025% (w/v) reagent solution sufficed for the maximum colour intensity of 0.25 μg Ti/ml in a total volume of 25 ml.

The titanium–methyl fluorone complex is quite stable for over 24 h at room temperature and within that period shows no change in the absorption value.

Beer's law curve

The O. D.–concentration curve is a straight line passing through the origin. From 0.025 to 0.6 p.p.m. of titanium the O. D. increases linearly with concentration in accordance with Beer's law.

The optimum range and accuracy of the proposed method were determined as described earlier[9]. The optimum range (Fig. 4) is from 0.1–0.6 p.p.m. of titanium, where the relative analysis error per 1% absolute photometric error is 3.1%.

Effect of foreign ions

Chloride, nitrate, perchlorate, sulphate, acetate, ferrous, uranyl, thorium, chromium, aluminium, potassium, sodium and alkaline earths in reasonable amounts did not interfere with the determination, while fluoride, oxalate, tartrate, citrate, phosphate, ceric and cerous, ferric, vanadate and chromate interfered. Ferric and vanadate ions, if masked by ascorbic acid before the addition of the reagent, could be tolerated even up to 30 p.p.m. and 10 p.p.m. respectively.

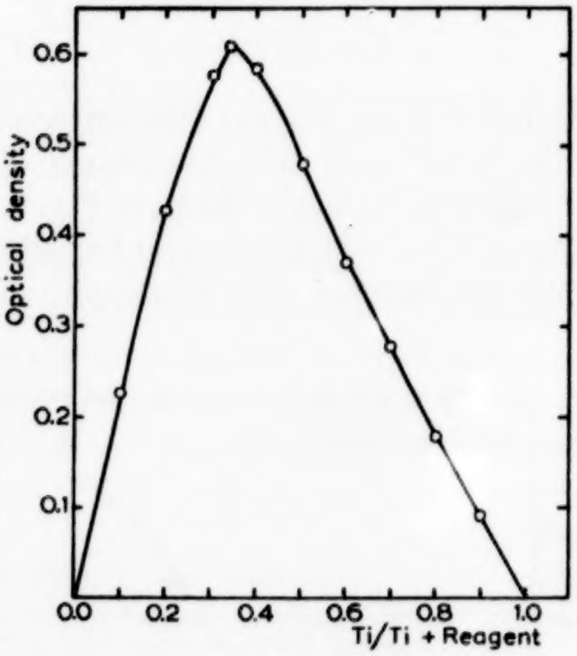

Fig. 5. Job's method of continuous variation.

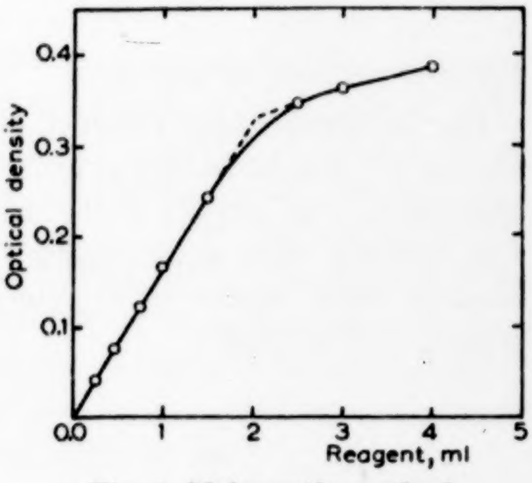

Fig. 6. Molar ratio method.

Composition of the complex

For the elucidation of the composition of the complex by Job's method the absorptions of mixtures (12 ml) of equimolecular solutions ($1 \cdot 10^{-4}$ M) of titanium and reagent were measured at 520 mμ, the total volume being kept constant at 25 ml by water. Fig. 5 shows the corrected absorption plotted against increasing amounts of titanium; the peak of the curve indicates compound formation at the metal to reagent ratio of 1:2. The molar ratio method supports this finding (Fig. 6).

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Extinction coefficient, sensitivity, degree of dissociation and instability constant

The molar extinction coefficient of the complex calculated from Beer's law is

$$\frac{0.315 \cdot 47.9 \cdot 10^3}{0.25} = 60360.$$

The sensitivity of the reaction according to SANDELL's definition is 0.00079 μg/cm^2.

Since 1 mole of titanium reacts with 2 moles of methyl fluorone to form 1 mole of the complex, the instability constant, K, is evaluated from the equation

$$K = \frac{ac\,(2ac)^2}{c(1-a)} = \frac{4\,a^3c^2}{1-a}$$

where c is the concentration of the complex in moles per l and a is the degree of dissociation. The value of a is obtained from the relationship[9]

$$a = \frac{E_m - E_s}{E_m}.$$

The E_m and E_s values are equal to 0.315 and 0.238 respectively at a titanium concentration of $5.198 \cdot 10^{-6}\,M$; thus the degree of dissociation a, equals 0.2444 and K is $1.6 \cdot 10^{-12}$.

ACKNOWLEDGEMENT

The authors wish to thank the University Grants Commission, Government of India, for providing the instruments used.

SUMMARY

9-Methyl-2,3,7-trihydroxy-6-fluorone is described as a highly sensitive reagent for titanium. The rose-red complex gives maximum absorption at 520 mμ and obeys Beer's law from 0.025–0.6 p.p.m. of titanium. The optimum concentration range is from 0.1–0.6 p.p.m. of titanium, where the relative error is 3.1%. The complex in solution has a metal to reagent ratio of 1:2. The molar extinction coefficient and the instability constant of the complex are about 60360 and $1.6 \cdot 10^{-12}$.

RÉSUMÉ

Les auteurs proposent la méthyl-9-trihydroxy-2,3,7-fluorone-6 pour le dosage spectrophotométrique du titane. Réactif très sensible; le complexe obtenu est rouge rose avec absorption maximum à 520 mμ; coefficient d'extinction moléculaire 60360.

ZUSAMMENFASSUNG

Als sehr empfindliches Reagenz zur spektrophotometrischen Bestimmung von Titan hat sich Methyl-9-trihydroxy-2,3,7-fluoron-6 erwiesen. Der gebildete rosa-rote Komplex besitzt ein Absorptionsmaximum bei 520 mμ und einen molekularen Extinktionskoeffizienten von 60360.

REFERENCES

[1] J. XAVIER, A. K. CHAKRABURTTY AND P. RAY, *Proc. Indian Sci. Congr.*, 42 (1955) 77.

[2] W. F. HILLEBRAND AND G. E. F. LUNDELL, *Applied Inorganic Analysis*, John Wiley and Sons, Inc., New York 1950, p. 456.

[3] F. D. SNELL AND C. J. SNELL, *Colorimetric Methods of Analysis*, Vol. II, D. Van Nostrand Co., Inc., New York 1954, p. 438.

[4] *Analytical Chemistry of the Manhattan Project*, edited by C. J. RODDEN, McGraw-Hill Book Co., Inc., New York 1950, p. 471.

[5] *Analytical Chemistry of the Manhattan Project*, edited by C. J. RODDEN, McGraw-Hill Book Co., Inc., New York 1950, p. 474.

[6] J. H. YOE AND A. R. ARMSTRONG, *Anal. Chem.*, 19 (1947) 100.

[7] T. C. J. OVENSTON, C. A. PARKER AND C. G. HATCHARD, *Anal. Chim. Acta*, 6 (1952) 7.

[8] V. DAMODARAN, *J. Sci. Ind. Research* (India), 16B (1957) 366.

[9] A. K. MAJUMDAR AND C. P. SAVARIAR, *Anal. Chim. Acta*, 21 (1959) 146.

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Short Communication

A note on the relative density of mixtures of water and *n*-butanol within the butanol rich range.

The author recently required the relative densities of mixtures of *n*-butanol and water, the composition of the samples lying within the butanol rich range. These were available only at 20° from the International Critical Tables[1] and from WAD AND GOKHALE[2] for 30°. Rather than interpolate values, it was decided to make fresh determinations. It was found, however, that there was a reasonable agreement between the determined and interpolated values.

n-Butanol was prepared from a commercially pure source by fractionating, using a glass column, 60 cm by 5 cm, filled with small glass rings (0.8 cm × 1.0 cm O.D.). The fraction boiling between 116° and 117° at 755 mm pressure was selected for use. A Schiff's test showed it to be substantially free from aldehydes. The water was doubly distilled from glassware then boiled, to remove dissolved gases, and cooled immediately before the mixtures were prepared. The relative densities were determined using a pyknometer with the temperature controlled to 25° ± 0.1 in a thermostat bath. The results are given in Table I.

TABLE I

X	Y	*90% confidence limits of* $\mu_Y(X)$
1.494	0.81144	0.00012
2.899	0.81421	0.00011
4.213	0.81672	0.00010
5.660	0.81951	0.00008
6.968	0.82198	0.00007
8.227	0.82436	0.00006
9.443	0.82658	0.00006
10.808	0.82910	0.00007
11.938	0.83130	0.00008
13.070	0.83340	0.00009
14.244	0.83577	0.00010
15.392	0.83749	0.00012

X represents the percentage by weight of water in *n*-butanol. Y is the relative density as determined for the solution of composition X.

The data obtained in the above manner was submitted to a statistical analysis along the following lines. A straight line relationship was assumed between the percentage of water by weight in *n*-butanol and the relative density of the solution at 25°. This may be represented as

$$\mu_Y(X) = \alpha + \beta X$$

where X is the water content in percent, $\mu_Y(X)$ is the true value of the relative density at a particular water content and α and β are constants. If Y represents the

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determined value for relative density of a solution of composition X, the deviations from the means, $x = X - X$ and $y = Y - Y$, may be found, and from them the constants a and b of the least-squares equation $\hat{Y} = a + bX$
where a $(= Y - bX)$ and $b = (\Sigma xY / \Sigma x^2)$ estimate α and β respectively.

Thus $\hat{Y}$ may be taken as the best estimate of the true relative density, $\mu_Y(X)$ for the mixture of composition X. It is assumed that X is an independent variable having controlled values and Y is a normal variate.

The values of a and b found from the data in Table I were $a = 0.80879$ and $b = 0.0018831$.

To obtain the standard error of estimate, S_e, of the least-squares line, the value of $\Sigma Y^2 = \Sigma \hat{y}^2 - b\Sigma xy$ was calculated, where $y = Y - \hat{Y}$ and hence

$$S_e = \sqrt{\frac{\Sigma \hat{y}^2}{n-2}}$$

for n observation. This value was found to be 0.00012.

The 90% confidence limits of α and β were calculated from these expressions and had the values which follow them.

$$\text{for } \alpha = a \pm t_{0\cdot 1,\, n-2,}\, S_e \sqrt{\left(\frac{1}{n} + \frac{X^2}{\Sigma x^2}\right)} = \pm\, 0.00014$$

$$\text{for } \beta = b \pm t_{0\cdot 1,\, n-2,}\, S_e / \sqrt{\Sigma x^2} = \pm\, 0.000017$$

For the above calculation t was taken as 1.812 a value obtained from DAVIES[3].

The 90% confidence limits of $\mu_Y(X)$ did not deviate sufficiently from the determined values to make it worth while graphing them; they are therefore shown in Table I.

The value of a (= 0.80879) agrees very closely with the specific gravity of pure n-butanol at 25°C/25°C, a value of 0.80878 as calculated from data in the International Critical Tables[4].

The author's thanks are due to Mr. P. D. LARK for his generous help with the statistical work.

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[1] *International Critical Tables,* 3 (1926) 112.
[2] Y. D. WAD AND A. G. GOKHALE, *J. Indian Inst. Sci.*, 4 (1921) A; *C.A.*, 15 (1921) 2760^1.
[3] O. L. DAVIES, Ed, *Statistical Methods in Research and Production,* Oliver and Boyd, London 1957.
[4] *International Critical Tables,* 3 (1926) 28.

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REVUE DE LIVRE

Colorimetric methods of analysis, including photometric methods, par F. D. Snell, C. T. Snell et C. A. Snell, volume II A., D. van Nostrand Company Inc. Princeton, New Jersey 1959, 793 p., 32 fig., 112 s., 6 d.

F. A. Snell et C. T. Snell sont les auteurs d'un traité de colorimétrie en 4 vol. Ils viennent d'en faire paraître un 5ème, le volume II A, qui complète le volume II sur l'analyse colorimétrique inorganique. Il renferme donc toutes les méthodes établies depuis la parution du volume II. Je dis toutes, car les auteurs ont fait une bibliographie extrêmement complète des années 1947 à 1956. C'est une formule très heureuse étant donné la foule considérable de travaux qui paraissent dans ce domaine. Au lieu de refondre complètement leur livre, les auteurs ont préféré le compléter, de telle sorte que les volumes II et II A forment un tout cohérent, extrêmement bien documenté, le premier volume gardant toute sa valeur, avantage qui sera apprécié de tous ceux qui s'efforcent d'avoir une bibliothèque à l'ordre du jour.

En consultant le volume II A, on se rend compte de l'importance toujours plus grande que prennent les méthodes colorimétriques dans la science moderne, grâce aux remarquables avantages qu'elles présentent. Les auteurs ont su, et la chose n'était pas facile, classer, ordonner tous ces travaux. On y trouve, non seulement les méthodes d'analyse mais aussi les mises en solutions, les séparations, l'effet des ions gênants et la façon d'éliminer ces derniers. De plus des méthodes complètes d'analyse sont proposées pour divers échantillons: alliages, liquides biologiques, minerais, silicates, etc. Chacune d'elles y est brièvement exposée mais de façon précise si bien qu'il n'est pas toujours nécessaire de recourir aux références bibliographiques. En résumé un excellent ouvrage.

D. Monnier (Genève)

ERRATA

Analytica Chimica Acta, Vol. 20 (1959) page 337, Table I: The second equation under "*Three ions present*" should read:

$$(\mathrm{Ni}) \cdot 10^5 = 11.6\ A_{s640} + 4.08\ A_{s440} - 4.50\ A_{s385}$$

instead of:

$$(\mathrm{Ni}) \cdot 10^5 = 11.6\ A_{s640} - 4.08\ A_{s440} - 4.50\ A_{s385}$$

Analytica Chimica Acta, Vol. 21 (1959), page 57, in the references. Reference 4 should have as its first author Fritz Will instead of W. Fitz.